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(54) Title: LITHOGRAPHIC PRINTING WITH POLARIZED LIGHT

(57) Abstract: The present invention provides systems and methods for improved lithographic printing with polarized light. In embodiments of the present invention, polarized light (radially or tangentially polarized) is used to illuminate a phase-shift mask (PSM) and produce an exposure beam. A negative photoresist layer is then exposed by light in the exposure beam. A chromeless PSM can be used. In further embodiments of the present invention, radially polarized light is used to illuminate a mask and produce an exposure beam. A positive photoresist layer is then exposed by light in the exposure beam. The mask can be an attenuating PSM or binary mask. A very high image quality is obtained even when printing contact holes at various pitches in low k applications.

WO 2004/077154 A2

## LITHOGRAPHIC PRINTING WITH POLARIZED LIGHT

## BACKGROUND OF THE INVENTION

## Field of the Invention

[0001] The present invention relates to high numerical aperture and immersion lithography.

## Related Art

[0002] Lithographic tools and techniques are increasingly called upon to print patterns at a high resolution. For example, in the manufacture of semiconductor dies or chips, patterns of circuit features, such as lines, contact holes, or other elements, often need to be printed at a high resolution to improve the packing density of circuit elements and reduce the pitch of the pattern. Certain circuit features, such as contact holes or vias, are especially difficult to fabricate.

[0003] A well-known parameter relating to lithography resolution is the critical dimension (CD). The CD is the size of the smallest geometrical features which can be formed during semiconductor device and circuit manufacturing using a given technology. The critical dimension can be described as shown in the following function:

$$CD = k (\lambda / NA),$$

where  $\lambda$  is a wavelength used in lithography, NA is the numeric aperture, and k is the dielectric constant. Among the trends in lithography is to reduce the CD by lowering the wavelength used, increasing the numeric aperture, and reducing the value k.

[0004] Printing can be difficult in low k applications. For example, contact holes are difficult to print when k is less than 0.5. A high-contrast image of sufficient quality that includes groups of contacts holes like contact arrays is especially hard to print.

- 2 -

[0005] Techniques to enhance contrast using a very high NA and off-axis illumination have been used but these techniques fail for small pitches. For example, at 157 nm wavelength, 0.93 NA, the limiting pitch (based on resolution) is roughly 135 nm ( $k=0.4$ ) – which is too high for certain applications. Also, a forbidden pitch may occur. This means that if the illumination is optimized for a given pitch, printing other pitches simultaneously may become impossible. Forbidden pitch can be manifested in a low normalized image log slope (NILS) or poor CD control for the forbidden pitch.

#### SUMMARY OF THE INVENTION

[0006] The present invention provides systems and methods for improved lithographic printing with polarized light.

[0007] In embodiments of the present invention, polarized light (for example, radially, tangentially, or custom polarized) is used to illuminate a phase-shift mask (PSM) and produce an exposure beam. A negative photoresist layer is then exposed by light in the exposure beam. A chromeless PSM can be used. In one example embodiment, radially polarized light is used in conjunction with chromeless PSMs, Cartesian quadrupole (C-quad) illumination and negative photoresists. A very high image quality is obtained even when printing contact holes at various pitches in low  $k$  applications. Forbidden pitch is avoided.

[0008] In further embodiments of the present invention, radially polarized light is used to illuminate a mask and produce an exposure beam. A positive photoresist layer is then exposed by light in the exposure beam. The mask can be an attenuating PSM or binary mask. In one example embodiment, radially polarized light is used in conjunction with attenuating phase-shift masks or binary masks, standard diagonal quadrupole illumination and positive photoresists. A very high image quality is obtained even when printing contact holes at various pitches in low  $k$  applications.

- 3 -

[0009] To further improve printing, a custom polarization can be used. The custom polarization may be, for example, a combination of radial and tangential polarization. In addition, an alternating PSM can also be used to improve print quality.

[0010] Further embodiments, features, and advantages of the present inventions, as well as the structure and operation of the various embodiments of the present invention, are described in detail below with reference to the accompanying drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS/FIGURES

[0011] The accompanying drawings, which are incorporated herein and form a part of the specification, illustrate the present invention and, together with the description, further serve to explain the principles of the invention and to enable a person skilled in the pertinent art to make and use the invention.

[0012] **FIG. 1** is a lithography system according to an embodiment of the present invention.

[0013] **FIG. 2** is a lithography system according to an embodiment of the present invention.

[0014] **FIG. 3A** is a zoomed-in image of contact holes in resist on a wafer.

[0015] **FIG. 3B** is a top-view image of contact holes in resist on a wafer.

[0016] **FIGS. 4A and 4B** illustrate 2D attenuating PSM mask spectra,  $p_x = p_y = p$  with on-axis and off-axis illumination respectively according to an embodiment of the present invention.

[0017] **FIG. 5** is an image that shows a limiting pitch with unpolarized light, where  $C_0$  and  $C_{45}$  are the orthogonal and diagonal contrasts, respectively.

[0018] **FIG. 6** is an illustration of an example simulation experiment (radially polarized light is shown for illustration).

[0019] **FIGS. 7A and 7B** show effects of radial and tangential polarization on image quality.

- 4 -

[0020] FIGS. 8A - 8C show a comparison of three polarization modes in an example of 125-nm pitch (45-degree-rotated masks).

[0021] FIGS. 9A - 9C illustrate effects of polarization on image quality. FIG. 9A illustrates a poor contrast image of grouped contact holes obtained in a case using unpolarized light. FIG. 9B illustrates a poor contrast image of grouped contact holes obtained in a case using tangentially polarized light. FIG. 9C illustrates a high contrast image of grouped contact holes obtained in a case using radially polarized light according to an embodiment of the present invention.

[0022] FIG. 10A illustrates the effect of a tangential polarizer on electric field vectors in light.

[0023] FIG. 10B illustrates the effect of a radial polarizer on electric field vectors in light.

[0024] FIGS. 11A and 11B are diagrams that show through pitch behavior using radially polarized light with a chromeless, alternating PSM according to an embodiment of the present invention.

[0025] FIG. 12 is an illustration of an attenuating PSM.

[0026] FIG. 13 is an illustration of a binary PSM.

[0027] FIGS. 14A - 14C are images that show effects of polarization on image quality in the case of an attenuating PSM, 125 nm pitch according to an embodiment of the present invention.

[0028] FIG. 15 is an illustration of an alternating PSM.

[0029] FIG. 16 shows a chromeless alternating PSM mask layout.

[0030] FIGS. 17A and 17B show diffraction patterns for the 2D chromeless alternating PSM for on-axis and off-axis illumination respectively. FIG. 5 is an image that shows a limiting pitch with unpolarized light, where  $C_0$  and  $C_{45}$  are the orthogonal and diagonal contrasts, respectively.

[0031] FIGS. 18A and 18B show images in air (a) and in resist (b) using an example chromeless alternating PSM.

[0032] FIGS. 19A, 19B and 19C show six aerial images at best focus vs. pitch using chromeless alternating PSMs and radially polarized light with C-quad.

- 5 -

- [0033] **FIGS. 20A and 20B** are graphs that show aerial image characteristics versus pitch.
- [0034] **FIGS 21A and 21B** are example custom polarization maps.
- [0035] **FIG. 22** is an immersion image in the case of unpolarized light with diagonal quadrupole and 6% attenuating PSM at  $n = 1.5$ .
- [0036] **FIG. 23** is an aerial image at best focus under extreme ultraviolet radiation (EUV) conditions.
- [0037] The present invention will be described with reference to the accompanying drawings. The drawing in which an element first appears is typically indicated by the leftmost digit(s) in the corresponding reference number.

## DETAILED DESCRIPTION OF THE INVENTION

### TABLE OF CONTENTS

#### *1. Overall System*

#### *2. Discussion and Simulation Results*

##### *A. Introduction*

##### *B. Resolution*

###### *B.1. Theoretical resolution limits*

###### *B.2. Resolution capability with off-axis illumination lithography*

##### *C. Polarization*

###### *C.1. Simulation Experiment*

###### *C.2. Effect of Polarization on Image Quality*

###### *C.3. Polarized light, Chromeless PSM, Negative photo-resist*

###### *C.4. Radially polarized light, attenuating phase-shift masks or binary masks, and positive photoresists*

##### *D. Polarization With Chromeless Alternating PSM*

###### *D.1. Chromeless Alternating PSM In Conjunction With Radially Polarized Light, 100-nm Pitch Nested Contacts*

- 6 -

***D.2. Through-Pitch Behavior, Chromeless Contacts With Radially Polarized Light***

***D.3. Custom Polarization***

***E. Immersion Lithography***

***F. EUV***

[0038] While specific configurations and arrangements are discussed, it should be understood that this is done for illustrative purposes only. A person skilled in the pertinent art will recognize that other configurations and arrangements can be used without departing from the spirit and scope of the present invention. It will be apparent to a person skilled in the pertinent art that this invention can also be employed in a variety of other applications.

[0039] The present invention provides systems and methods for improved lithographic printing with polarized light.

***1. Overall System***

[0040] FIG. 1 is a lithography system 100 according to an embodiment of the present invention. System 100 includes an illumination source 102. In an embodiment, illumination source 102 emits pre-polarized illumination light along an optical path. Although the present invention is described herein with reference to pre-polarized illumination light, one of skill in the art will recognize that unpolarized illumination light may also be used. For example of pre-polarized light, illumination source 102 can be a laser that emits a laser beam with a tendency to be approximately linearly polarized. Alternatively, a polarizer could be added within a laser generator in polarized illumination source 102.

[0041] The pre-polarized light then passes through a pattern polarizing device 104. As used herein, pattern polarizing device 104 is defined to encompass any polarizing device including, but not limited to, traditional and custom

- 7 -

polarizers and wave plates. If pre-polarized light is emitted by illumination source 102, pattern polarizing device 104 may be any polarizing device such as, for example, one or more of a polarizer or a wave plate. If unpolarized light is emitted by illumination source 102, pattern polarizing device 104 is a polarizer rather than a wave plate.

[0042] Pattern polarizing device 104 shapes the pre-polarized illumination light into various predetermined arrangements, such as polarization patterns and intensity patterns. For example, pattern polarizing device 104 may shape the pre-polarized illumination light into radially polarized light, tangentially polarized light, or light with a custom polarization. In an embodiment, the illumination light is quadrupole illumination, such as Cartesian quadrupole (C-quad) illumination. Although quadrupole illumination is used herein as an example, one of skill in the art will recognize that illumination of any source shape may be used.

[0043] The illumination light illuminates mask 106. Mask 106 produces a design in the illumination light. One of skill in the art will recognize that mask 106 can be any type of mask or reticle. In an embodiment of the present invention, mask 106 is a binary mask. In other embodiments, mask 106 is a phase-shift mask (PSM), such as, for example, a chromeless PSM, alternating PSM, or attenuating PSM.

[0044] The light including the mask design then passes through projection optic 108, which further conditions and processes the light. Projection optic 108 may include one element or a plurality of optical elements. Projection optic 108 produces an exposure beam that continues along the optical path.

[0045] Finally, the exposure beam exposes wafer 110 according to the design carried by the exposure beam. In embodiments of the present invention, wafer 110 is covered by a negative photoresist layer. In one example embodiment, radially polarized light is used in conjunction with chromeless PSMs, C-quad illumination and negative photoresists. A very high image quality is obtained even when printing contact holes at various pitches in low k applications. Forbidden pitch is avoided.



- 8 -

[0046] In other embodiments of the present invention, wafer 110 is covered by a positive photoresist layer. For example, radially polarized light is used in an embodiment to illuminate mask 106 and produce an exposure beam. A positive photoresist layer is then exposed by light in the exposure beam. In another embodiment, radially polarized light is used in conjunction with attenuating phase-shift masks or binary masks, standard diagonal quadrupole illumination and positive photoresists. A very high image quality is obtained even when printing contact holes at various pitches in low k applications.

[0047] FIG. 2 is another example lithography system 200 in which the present invention can be implemented. Polarized illumination source 102 and mask 106 perform the same functions as described with respect to system 100. In system 200, however, a pattern polarizing device 202 is included in projection optic. As with pattern polarizing device 104, pattern polarizing device 202 shapes the pre-polarized illumination light into various predetermined arrangements, such as a radial polarization arrangement, a tangential polarization arrangement, or a custom polarization arrangement. Optical components for further shaping and conditioning the illumination light may be placed before and/or after pattern polarizing device 202. These optical components are shown as projection optic 204A and projection optic 204B, and create an exposure beam that continues along the optical path..

[0048] After being shaped by pattern polarizing device 202 and projection optics 204A and/or 204B, the polarized light exposes wafer 110 according to the design produced by mask 106. As stated with respect to FIG. 1, wafer 110 may be covered with either a positive or negative photoresist layer.

## ***2. Discussion and Simulation Results***

[0049] The following discussion and simulation results is provided to further illustrate aspects and features of embodiments of the present invention, and is not intended to limit the present invention. The inventors compared several approaches to printing 50/50-nm nested contact holes using the Prolith™ 7.1

- 9 -

lithography simulation system available from KLA-Tencor Corp. The approaches used include: off-axis quadrupole illumination and attenuating phase-shift mask with optimized polarization of the illumination; chromeless alternating phase shift-masks (CAPSM) in conjunction with special polarization schemes; immersion lithography with extremely high numerical aperture (NA) at 157-nm wavelengths; and EUV lithography.

[0050] The inventors found the limits of the off-axis illumination technique can be pushed with the use of radial polarization and how the mask bias (or background transmission) can be used to optimize the image. Resolution limits are further pushed with 2D chromeless alternating PSM combined with the radial polarization. With radial polarization enhancement according to embodiments of the present invention, high-contrast images can be obtained and high-quality contact holes at 100-nm pitch can be printed using negative photo-resist. Radial polarization according to embodiments of the present invention can further enhance image quality in example applications involving immersion. The inventors further compared these findings with results obtained at an extreme ultraviolet radiation (EUV) wavelength to confirm that imaging at an EUV wavelength and low NA can also provide excellent conditions to print 100-nm-pitch contact holes.

#### *A. Introduction*

[0051] At present, producing 50-nm contacts with a 100-nm pitch represents a challenge for optical lithography. Industry roadmaps for semiconductor devices require 50 nm contacts to be available by 2008. To achieve this capability before EUV becomes widely available requires a significant extension to current optical lithography. Even with high-NA optics using a 157-nm wavelength, traditional contrast-enhancement techniques such as off-axis illumination and attenuating PSM are not sufficient to print 100-nm-pitch

- 10 -

contact holes of a high enough quality. There is a need to use resolution-enhancing techniques in addition to quadrupole illumination with attenuating PSM for the printing of 100-nm-pitch contacts. For reference, **FIG. 3A** is a zoomed-in diagram of an example wafer with contact holes. Resist layer 302 is attached to wafer surface 304. A lithography system (not shown) exposes resist layer 302 to produce contact hole 306. **FIG. 3B** is an image of the contact hole pattern when viewed from above.

[0052] Simulations were used to examine the optimum printing technique for grouped contacts according to embodiments of the present invention. The inventors used Prolith<sup>TM</sup> 7.1 to explore techniques to improve contact-window printing capabilities. First, the inventors simulated conventional lithographic conditions for a high numerical aperture 157-nm system and establish the minimum pitch that can be printed with adequate image contrast. Next, the inventors progressively modified the technique to improve resolution capability. In this way, the present inventions demonstrates an improvement in results compared with the starting condition of off-axis illumination and a 6% attenuated phase-shift mask (PSM) by first optimizing the polarization of the illumination, exploring chromeless phase-shift masks, and then by introducing wavelength-shortening methods such as immersion lithography and EUV lithography.

## ***B. Resolution***

[0053] First, the theory of resolution is examined in the context of printing contacts. This theory helps explains how one can enhance the resolution of system for contact arrays.

### ***B.1. Theoretical resolution limits***

- 11 -

- [0054] For a 2D periodic pattern of pitch  $p_x$  in the x direction and  $p_y$  in y direction, the mask spectrum is non zero at discrete spatial frequencies whose x and y components are inversely proportional to the pitch:

$$(f_x, f_y) = \left( \frac{n}{p_x}, \frac{m}{p_y} \right)$$

where n and m are integer numbers (0, +/-1, +/-2, +/- 3 etc.)

- [0055] Often, it is more convenient to work with normalized spatial frequencies i.e.:

$$(\hat{f}_x, \hat{f}_y) = \left( \frac{n\lambda}{p_x \cdot NA}, \frac{m\lambda}{p_y \cdot NA} \right)$$

- [0056] At a minimum, in addition to the zero order, the first three diffraction orders must be captured by the lens to ensure sufficient resolution, i.e., the (0,0), (0,1), (1,0) and (1,1) orders.

- [0057] For on-axis illumination, this requirement is equivalent to:

$$\sqrt{\hat{f}_x^2 + \hat{f}_y^2} \leq 1$$

i.e., fitting a square into one quadrant of a unit radius circle (see diffraction pattern in **FIG. 4A**)

$$\text{i.e.} \quad p \geq \frac{\lambda}{NA} \cdot \sqrt{2} \quad \text{if} \quad p_x = p_y = p,$$

and with diagonal off-axis illumination:

$$\sqrt{\hat{f}_x^2 + \hat{f}_y^2} \leq 2$$

i.e., fitting a square into the entire unit radius circle (see diffraction pattern in **FIG. 4B**),

$$\text{i.e.} \quad p \geq \frac{\lambda}{NA} \cdot \frac{\sqrt{2}}{2} \quad \text{if} \quad p_x = p_y = p.$$

- [0058] By using this theory, one can establish that at 157-nm wavelength and 0.93 NA, and for grouped contact holes, the theoretical minimum pitch (in x and y directions) that can be imaged is therefore 240 nm with on-axis illumination and 120 nm with off-axis illumination. The inventors ran simulations to further explore the off-axis case.

***B.2. Resolution capability with off-axis illumination lithography***

[0059] Resolution can be improved by going from conventional on-axis illumination to off-axis illumination. Being able to produce an image is, by itself, insufficient to meet certain quality criteria to ensure sufficient process latitude in resist. To print nested contact holes, assume that contrast and normalized image log slope (NILS) must be greater than 0.5 and 1.5, respectively. See, Graeupner, P., *et al.*, "Solutions for printing sub-100 nm contact with ArF," *SPIE 4691*:503 (2002).

[0060] With these requirements, the inventors determined the smallest pitch at which nested contact holes can be printed in this example. First, example high-quality conditions for printing low-k, grouped contact holes were considered. These conditions include:

- 0.9/0.1 Quadrupole illumination with diagonal poles (where 0.9 is the distance of the poles from the center and 0.1 is the pole radius)
- 0.93 NA
- 6% 1:1 Attenuating PSM
- Unpolarized light incident on the reticle

[0061] By gradually decreasing the pitch, the aerial image contrast in the pitch direction (C0) can stay above 0.5 as long as the pattern pitch is 134 nm (i.e. 67-nm contacts and spaces). This coincides with a NILS of ~1.5. The resulting image is shown in **FIG. 5**.

[0062] The printing resolution pitch of contacts can be improved from 240 nm to 134 nm by changing from on-axis illumination to off-axis illumination. Clearly, the smallest resolvable pitch as defined above will change somewhat when using a slightly different NA or quadrupole. This definition does not take into account depth of focus (DOF); therefore, the lowest printable pitch is expected to be larger. This example is sufficient to show that fairly unconventional means must be used to push the resolution limit down to 100-nm pitch.

### *C. Polarization*

- [0063] There are references in the literature to "polarization matching" in which the electric field vectors overlap and result in maximum interference and consequently in maximum image quality. See, Ma, Z., *et al.*, "Impact of illumination coherence and polarization on the imaging of attenuated phase shift masks," *SPIE 4346*:1522 (2001). Linearly polarized illumination has been used to improve image quality for lines of appropriate orientation, but no specific polarization schemes have been suggested for contact holes as in embodiments of the present invention.
- [0064] In the following discussion, the effects of using radially and tangentially polarized light are revealed. These two types of polarization enhance image quality for contact holes. Although radial and tangential polarizations are discussed here, one of skill in the art will recognize with this disclosure that other polarizations, including custom polarizations, can also be used to enhance image quality.
- [0065] Unless stated otherwise in the following, the NA is 0.93, the illumination is 0.9/0.1 diagonal quadrupole, and the wavelength is 157.6 nm.

#### *C.1. Simulation Experiment*

- [0066] The Prolith<sup>TM</sup> 7.1 simulator used for this work offered a choice of three polarization modes, namely, x polarized, y polarized, and unpolarized light. The image for the unpolarized mode was obtained by adding the aerial images of the x polarized and y polarized modes.
- [0067] To simulate tangentially or radially polarized light, a simple manipulation of the mask orientation was carried out using Prolith<sup>TM</sup> 7.1. An example of the orientation manipulation is illustrated in FIG. 6. Assuming the poles to be sufficiently small, the inventors first rotated the pattern by 45°.

- 14 -

They then calculated a first image using x-oriented dipole illumination with x or y polarized light (x polarization for radial and y polarization for tangential). Next, a second image was calculated using y-oriented dipole illumination with x or y polarized light (y polarization for tangential and x polarization for radial). Finally, the two images were added to obtain the final image.

### *C.2. Effect of Polarization on Image Quality*

[0068] For comparison, **FIGS. 7A** and **7B** show images using radial and tangential polarization, respectively, according to the present invention. The difference between tangential polarization and radial polarization is illustrated in **FIGS. 10A** and **10B**. When light is unpolarized, as shown in view 1002, the directions of the polarization vectors vary randomly. Once the unpolarized light passes through tangential polarizer 1004, however, the light becomes tangentially polarized, as shown in view 1006. Once they are tangentially polarized, the polarization vectors uniformly circle around a central location.

[0069] Radial polarization acts somewhat differently. As illustrated in **FIG. 10B**, when unpolarized light 1002 passes through radial polarizer 1008, the light becomes radially polarized light 1010. Once radially polarized, the polarization vectors emanate uniformly from the central location.

[0070] The pitch direction is shown as a diagonal line on **FIGS. 7A** and **7B**. The contrast along the pitch direction is very high, i.e., 0.88 with radial polarization, while it is very low (0.19) with tangential polarization. At 45 degrees from the pitch direction, contrast is high for both types of polarization.

[0071] With radially polarized light, the image can be optimized by changing the contact-hole width (i.e., the mask bias) until the contrast is the same in both the orthogonal and the diagonal directions (with tangential polarization, no such improvement was observed). A contact-hole width of 85 nm (i.e., 18-nm mask bias) produced uniform contrast at a pitch of 134 nm (approximately equal diagonal and orthogonal contrasts), in one preferred example.

- 15 -

[0072] Alternatively, it is possible to modify the background transmittance of the mask to obtain the same effect. The inventors found that radially polarized light results in an image quality that is superior to that produced with unpolarized light, even when out of focus.

[0073] The improved resolution afforded by the optimization of illumination polarization was examined. The minimum pitch can be reduced to 125 nm, and an optimum contact-hole width found. With radial polarization, intense side lobes can be observed at small contact-hole widths. The side lobes disappear as the contact-hole width is gradually increased from 50 nm to 75 nm. This is followed by a more uniformly distributed contrast around the contact. The results indicated that the radially polarized case offers more than 30% NILS improvement over the unpolarized light case. **FIGS. 8A - 8C** illustrate the comparison of the three polarization states according to the present invention. In each of these figures, the pitch direction is shown. **FIG. 8A** is an aerial image using unpolarized quadrupole illumination at 75 nm contact width. **FIG. 8B** is an aerial image with 75 nm contact width using tangentially polarized quadrupole illumination. Finally, **FIG. 8C** is an aerial image, again at 75 nm contact width, using radial quadrupole illumination.

[0074] Polarizing the illumination can improve the resolution limit from 134 nm down to 125 nm. These figures are based on the use of radially polarized light and a minimum contrast requirement of 0.5 (NILS requirement of 1.5).

### ***C.3. Polarized light, Chromeless PSM, Negative photo-resist***

[0075] In embodiments of the present invention, polarized light (radially or tangentially polarized) is used to illuminate a phase-shift mask (PSM) and produce an exposure beam. A negative photoresist layer is then exposed by light in the exposure beam. A chromeless PSM can be used. In one example embodiment, radially polarized light is used in conjunction with chromeless PSMs, Cartesian quadrupole (C-quad) illumination and negative photoresists. A very high image quality is obtained even when printing grouped or nested contact holes in low k applications. Forbidden pitch is avoided.



- 16 -

[0076] In one example, radially polarized light is used in conjunction with chromeless PSMs, Cartesian quadrupole illumination, and negative photo-resists to push the resolution to  $k=0.29$ . The present invention is not limited to Cartesian quadrupole illumination. Further examples include but are not limited to quasar illumination, illumination having four-fold symmetry, or any other illumination approximating quadrupole illumination. According to simulations performed by the inventors on the PROLITH™ 7.1 system, near perfect contrast of image occur when negative photo-resist and radially polarized illumination are used.

[0077] **FIGS. 9A - 9C** show the effect of polarization on image quality in the simulation results obtained by the inventors. The results shown in **FIGS. 9A - 9C** are simulations of 100 nm pitch, chromeless PSM contact holes using a 157 nm wavelength, 0.93 NA and a resist with a refractive index of 1.78. **FIG. 9A** shows a poor contrast image of contact holes obtained in a case using unpolarized light and quadrupole illumination. **FIG. 9B** shows a poor contrast image of contact holes obtained in a case using tangentially polarized light and quadrupole illumination. **FIG. 9C** shows a high contrast image of contact holes obtained in a case using radially polarized light and quadrupole illumination according to an embodiment of the present invention.

[0078] The minimum contrast of the three types of polarization in this example is summarized below:

Polarization state	Minimum contrast
Unpolarized	0.67
Tangential	0.44
Radial	1.0

[0079] In addition, this technique has the potential to be used at even lower k-factor (e.g., where k equals 0.26 with contrast larger than 0.75)

[0080] This approach shows no forbidden pitch as demonstrated in **FIGS. 11A and 11B**. **FIGS. 11A and 11B** are graphs that respectively plot the CD (in nm) and NILS over a range of pitches between 100 and 900 nm, according

- 17 -

to the present invention. **FIGS. 11A and 11B** show that NILS does not drop below 2.9 for all simulated pitches (100 to 900 nm in 25 nm pitch steps) indicating that all pitches can be printed simultaneously with good exposure latitude.

***C.4. Radially polarized light, attenuating phase-shift masks or binary masks, and positive photoresists***

[0081] In further embodiments of the present invention, radially polarized light is used to illuminate a phase-shift mask (PSM) and produce an exposure beam. A positive photoresist layer is then exposed by light in the exposure beam. The mask can be an attenuating PSM or binary mask.

[0082] An example of an attenuating PSM 1200 is shown in **FIG. 12**. For ease of explanation, only cell 1202 of attenuating PSM 1200 is described. Central section 1204 of cell 1202 is an area of 100% transmission, meaning that all light of a certain phase passes through. For example, central section 1204 may transmit all light having a phase of 0°. Outer section 1204 of cell 1202 causes the attenuation, in that a lower percent of light of another phase is transmitted. For example, as shown in **FIG. 12**, outer section 1206 only allows 6% of light at a phase of 180° to pass through.

[0083] Alternatively, a binary PSM may be used in the present invention. **FIG. 13** illustrates an example binary PSM 1300. For ease of explanation, only cell 1302 of binary PSM 1300 is described. Much like central section 1204 of attenuating PSM 1200, central section 1304 of binary PSM 1300 allows 100% of light through. However, instead of allowing an attenuated degree of light to pass, outer section 1306 prevents all light from passing through. In other words, outer section 1306 has a 0% transmission rate.

[0084] In one example embodiment, radially polarized light is used in conjunction with attenuating phase-shift masks or binary masks, standard diagonal quadrupole illumination and positive photoresists. A very high image quality is obtained even when printing contact holes at various pitches in low k applications.

- 18 -

[0085] Simulations performed by the inventors on 125 nm pitch contact holes using a 6% attenuating PSM and diagonal quadrupole (0.9/0.1) illumination showed image improvement when radially polarized light was used. The results from this simulation are shown in FIGS. 14A - 14C. The results shown in FIG. 14 are also summarized in the following table:

Polarization state	Minimum Contrast	Minimum NILS*
Unpolarized	0.64	1.85
Tangential	0.58	1.77
Radial	0.69	1.94

\*NILS stands for Normalized Image Log Slope

The present invention is not limited to quadrupole illumination. Further examples include, but are not limited to, quasar illumination, illumination having four-fold symmetry, or any other illumination approximating quadrupole illumination.

#### ***D. Polarization With Chromeless Alternating PSM***

[0086] Further improvements in the resolvable pitch for contacts can be made by changing the mask from an attenuating phase-shift mask to an alternating phase shift mask while retaining the use of polarized light.

##### ***D.1. Chromeless Alternating PSM In Conjunction With Radially Polarized Light, 100-nm Pitch Nested Contacts***

[0087] The chromeless alternating PSM layouts chosen for this example study are of the checkerboard type in which the phase is alternated between, for example, 0° and 180°. A diagram of a chromeless alternating PSM 1500 is shown in FIG. 15. The center section of PSM 1500 is highlighted to showcase the different sections and phases. Sections 1502 and 1504 are areas that allow 100% of light to pass through with a phase of, for example, 0°. Sections 1506 and 1508 are areas that allow 100% of light to pass through at a

- 19 -

phase different from that of sections 1502 and 1504. For example, sections 1506 and 1508 may have a phase of  $180^\circ$ . Darkened area 1510 does not allow any light through. Therefore, its transmission is 0%.

[0088] The repeat pattern for printing 100-nm-pitch contact holes is composed of 100 nm transparent squares with alternating phases, as illustrated in FIG. 16. See, mask layouts in Levenson, M.D., *et al.*, "The vortex mask: making 80 nm contacts with a twist!," *SPIE 4889* (2002) and Grassman, A., *et al.*, "Contact hole production by means of crossing sudden phase shift edges of a single phase mask," International patent WO 01/22164 A1 (2001). The resulting diffraction pattern for this contact array, with on-axis illumination for the chromeless mask, is shown in FIG. 17A.

[0089] With on-axis illumination, no diffraction orders are captured by the lens because the (0,0), (1,0), and (0,1) orders are extinct. With off-axis illumination, according to an embodiment of the present invention, the (1,1) family of diffraction orders can be moved into the pupil, as illustrated in FIG. 17B. An image can be obtained with this setup. With one pole, the image is equivalent to a 1D grating. By combining x-poles with y-poles, a 2D image is produced. FIGS. 18A and 18B illustrated this 2D image. This image can be enhanced by using the optimum polarization for the two interfering diffraction orders from each pole (in the case shown in FIG. 17B, x-polarized light is the optimum). This is like radially polarized poles with a Cartesian quadrupole.

[0090] Simulations in air and resist (FIGS. 18A - B) were for NA of 0.93, wavelength 157.6 nm, and the illumination was Cartesian quadrupole (the diagonal quadrupole presents no advantage but can be used). The four poles were radially polarized. Both the simulations in air and resist showed nearly perfect contrast as long as the contact holes were printed in negative photo-resist. NILS (calculated in air only) was very high (larger than 3, as shown in FIG. 18A).

#### ***D.2. Through-Pitch Behavior, Chromeless Contacts With Radially Polarized Light***

[0091] "Forbidden" pitches in lithography have been described. See, Socha, R., *et al.*, "Forbidden pitches for 130 nm lithography and below," *SPIE* 4000:1140 (2000), and Shi, X., *et al.*, "Understanding the forbidden pitch phenomenon and assist feature placement," *SPIE* 4689:985 (2002). For a given illumination angle, the forbidden pitch lies in the location where the field produced by the neighboring features destructively interferes with the field of the main feature. Difficulties are encountered when attempting to print contact holes of a given size at different pitches. See, Graeupner *et al.* The inventors used common illumination conditions and a common threshold to mimic simultaneous exposure and to evaluate the extent of any overlapping process windows.

[0092] For this set of simulations, the size of the transparent phase squares that make up the chromeless mask (see FIG. 16) was gradually increased from 100 nm to 1000 nm in 25-nm steps. FIGS. 19A, 19B, and 19C show the various images resulting from simulations at best focus for 200-nm, 300-nm, 400-nm, 500-nm, 600-nm, and 1000-nm pitches.

[0093] As a result of the present invention, the image of the contact generally remains particularly sharp and does not vary significantly in size with pitch. This is because the contact forms at the corners of the phase squares. One threshold necessary to print 50 nm contacts at 100-nm pitch has been calculated and found to be 0.28. At this threshold, side lobes are seen to develop for pitches of between 400 nm and 500 nm (see FIG. 19B) and, hence, assist features are needed to prevent side lobes from printing at these particular pitches. Side lobes do not appear to be a problem at other pitches and assist features are therefore not required.

[0094] NILS and contact width have been calculated at the 0.28 threshold for all pitches (see FIGS. 20A and 20B, respectively). The contact width is the width of the image at the target threshold (0.28, in this case), and NILS is the log slope of the image width at the same threshold.

[0095] As shown in FIG. 20B, the contact width varies almost linearly with pitch for small pitches (approx. 200 nm); this is the regime in which the image

- 21 -

is just the sum of orthogonal 1D gratings. Beyond this range, more diffracted orders are accommodated in the pupil. Although not shown here, the depth of focus (DOF) shows a change from infinite (with ideal mask, point source, and wave front) to finite, when more diffracted orders contribute to the image.

[0096] As shown in **FIG. 20A**, the NILS for all pitches under consideration in this example remains well above 2.5. This indicates good exposure latitude for all pitches. Contact width, on the other hand, varies from 50 nm to 105 nm (worst pitch) and stabilizes at about 65 nm. This is quite remarkable and has advantages of the simplicity of the mask layouts and the absence of a pitch-dependent pattern and illumination optimization. Compare, Graeupner *et al.*, Socha, R., *et al.*, and Shi, X., *et al.*

### ***D.3. Custom Polarization***

[0097] In an embodiment, custom polarized light is used in place of simple radial or tangential polarized light. **FIG. 21A** is a map of an example custom polarization pattern, where each arrow represents the direction of the field vectors at a specific section of the light beam. **FIG. 21B** is another map of an example custom polarization pattern. Unlike radial or tangential polarization, custom polarization patterns have a non-uniform arrangement of polarization vectors. These polarization vectors are shown as arrows in **FIGS. 21A** and **21B**. In an embodiment, custom polarized light, as well as radial and tangential polarization, can be produced by a pattern polarizing device, such as pattern polarizing device 104 or 202. The pattern in the pattern polarizing device is predetermined, and the pattern polarization device can be changed as necessary to produce the desired polarization. The illumination configuration, or shape of the illumination light at the illumination source, can be customized as well. The ability to provide customized illumination, as well as customized polarization and intensity, optimizes printing.

### ***E. Immersion Lithography***

- 22 -

[0098] Another lithographic technique, immersion lithography, can also be used for the printing of contacts in the present invention. In immersion lithography at least the space between the projection optic, such as projection optic 108, and the wafer, such as wafer 110, is filled with a liquid. Using immersion lithography, it is possible to extend the pitch-resolution limits from 125 nm down to 100 nm. To simulate immersion lithography, the wavelength was scaled by the refractive index of the immersion liquid (e.g., 1.5). The liquid NA that could potentially be achieved with a suitable lens design is 1.395. **FIG. 22** is an image of 50-nm contact holes at a 100-nm pitch simulated with immersion lithography according to the present invention. The NILS is in excess of 1.74; this indicates that this is a viable optical lithography technique for 50-nm contacts on a 100-nm pitch.

#### *F. EUV*

[0099] EUV was also examined, as it affords very short wavelength and, hence, has a high k factor at 100-nm pitch. An aerial image simulation of the image using typical EUV conditions (0.6 PC, 0.25 NA, and a binary contact-hole mask with unpolarized light) confirms that EUV can print very high-quality 50nm contact images at 100 nm pitch. The result of a simulation using EUV according to the present invention is shown in **FIG. 23**.

[00100] NILS and contrast have both been found to be more than 0.7 and 2.5, respectively, over a 0.4-micron DOF; this indicates that EUV could, under the right conditions, provide robust imagery.

[00101] The inventors considered several approaches to the printing of 100-nm-pitch nested contact holes and found that 157-nm and high NA allows the printing of 134-nm-pitch contacts with good image quality. Further, radial polarization, in conjunction with a state-of-the-art approach at 157 nm (attenuated PSM, quadrupole, etc.), can result in a notable improvement compared with results produced using unpolarized light. The smallest pitch

- 23 -

resolved with this technique is 125 nm. With radial polarization, C-quadrupole, chromeless alternating PSM and negative photo-resist, one can obtain nearly perfect contrast images of 100-nm-pitch contact holes at 157 nm. The inventors found this approach to be by far the best at 157 nm. Image quality remained almost constant through pitch and the inventors did not observe a forbidden pitch. The inventors discovered that immersion, at 157 nm and in a 1.5 refractive index hypothetical fluid, results in high-quality images at 100-nm pitch, while EUV conditions result in very high-quality images for 100-nm-pitch contacts.

[00102] The simulation results are summarized in the table below.

Method	Wavelength (nm)	NA	Pitch (nm)	Contrast	NILS
Att PSM & unpolarized light	157.6	0.93	134	0.5	1.55
Att PSM & radial polarization	157.6	0.93	125	0.51	1.47
Chromeless PSM & radial polarization	157.6	0.93	100	0.99	3.08
Immersion	157.6	1.395	100	0.62	1.74
EUV	13.4	0.25	100	0.99	5.27

[00103] While various embodiments of the present invention have been described above, it should be understood that they have been presented by way of example only, and not limitation. It will be apparent to persons skilled in the relevant art that various changes in form and detail can be made therein without departing from the spirit and scope of the invention. Thus, the breadth and scope of the present invention should not be limited by any of the above-described exemplary embodiments, but should be defined only in accordance with the following claims and their equivalents.



- 24 -

WHAT IS CLAIMED IS:

1. A method for printing on a wafer, comprising:
  - (a) producing an exposure beam with polarized illumination light, wherein the illumination light is polarized according to a predetermined polarization pattern;
  - (b) illuminating a mask to produce an image in the exposure beam; and
  - (c) exposing a photoresist layer on the wafer with light in the exposure beam.
2. The method of claim 1, wherein said step (a) further comprises producing polarized illumination light according to a radial polarization pattern.
3. The method of claim 1, wherein said step (a) further comprises producing polarized illumination light according to a tangential polarization pattern.
4. The method of claim 1, wherein said step (a) further comprises producing polarized illumination light according to a custom polarization pattern.

- 25 -

5. The method of claim 1, wherein said step (a) further comprises producing polarized quadrupole illumination.
6. The method of claim 1, further comprising before said step (a):  
emitting pre-polarized light to produce illumination light.
7. The method of claim 1, wherein said step (b) comprises illuminating a mask to produce an image that includes contact holes.
8. The method of claim 1, wherein said step (c) occurs in a liquid.
9. The method of claim 1, wherein the mask is at least one of the group consisting of: chromeless phase-shift mask, attenuating phase-shift mask, and alternating phase-shift mask.
10. The method of claim 1, wherein the mask is a binary mask.
11. A method of printing on a wafer, comprising:
  - (a) producing an exposure beam with polarized illumination light, wherein the illumination light is

- 26 -

polarized according to a predetermined polarization pattern;

- (b) illuminating a chromeless phase-shift mask to produce an image in the exposure beam; and
- (c) exposing a negative photoresist layer on the wafer with light in the exposure beam.

12. A method of printing on a wafer, comprising:

- (a) producing an exposure beam with polarized illumination light, wherein the illumination light is polarized according to a predetermined polarization pattern;
- (b) illuminating an attenuating phase-shift mask to produce an image in the exposure beam; and
- (c) exposing a positive photoresist layer on the wafer with light in the exposure beam.

13. A method of printing on a wafer, comprising:

- (a) producing an exposure beam with polarized illumination light, wherein the illumination light is polarized according to a predetermined polarization pattern;
- (b) illuminating a binary mask to produce an image in the exposure beam; and

- 27 -

- (c) exposing a positive photoresist layer on the wafer with light in the exposure beam.
14. A method of printing on a wafer, comprising:
- (a) illuminating a phase-shift mask with pre-polarized light;
  - (b) shaping said pre-polarized light to produce an exposure beam, wherein the pre-polarized light is shaped according to a predetermined polarization pattern and intensity pattern; and
  - (c) exposing a photoresist layer on the wafer with the exposure beam.
15. A lithography system, comprising:
- (a) an illumination source that emits illumination light along an optical path;
  - (b) a pattern polarizing device that converts illumination light from the illumination source into an exposure beam with a predetermined polarization pattern;
  - (c) a mask that produces an image in the exposure beam;
  - (d) a projection optic that relays the exposure beam for printing on a wafer.

- 28 -

16. The lithography system of claim 15, wherein said illumination light is pre-polarized illumination light, and wherein said pattern polarizing device is a wave plate.
17. The lithography system of claim 15, wherein said illumination light is pre-polarized illumination light, and wherein said pattern polarizing device is a polarizer.
18. The lithography system of claim 15, wherein said illumination light is unpolarized illumination light, and wherein said pattern polarizing device is a polarizer.
19. The system of claim 15, further comprising:
  - (e) a wafer exposed by the exposure beam.
20. The lithography system of claim 19, further comprising a liquid filling a space between said projection optic and said wafer.
21. The lithography system of claim 15, wherein said pattern polarizing device is included in the projection optic.

- 29 -

22. The lithography system of claim 15, wherein said predetermined polarization pattern is a radial polarization pattern.
23. The lithography system of claim 15, wherein said predetermined polarization pattern is a tangential polarization pattern.
24. The lithography system of claim 15, wherein said predetermined polarization pattern is a custom polarization pattern.
25. The lithography system of claim 15, wherein said mask is one of the group consisting of: a chromeless phase-shift mask, an attenuating phase-shift mask, a binary mask, and an alternating phase-shift mask.
26. The lithography system of claim 15, wherein said image includes contact holes for a wafer.
27. A method of producing contact holes on a wafer, comprising:
  - (a) producing a polarized illumination beam;
  - (b) illuminating a mask with the polarized illumination beam to create an exposure beam, wherein said mask

- 30 -

produces a contact hole image in the exposure beam;  
and

(c) exposing a wafer with the exposure beam.

28. The method of claim 27, wherein said step (b) further comprises illuminating a phase-shift mask.
29. The method of claim 27, wherein said step (a) further comprises producing a radially polarized illumination beam.
30. The method of claim 27, wherein said step (a) further comprises producing a tangentially polarized illumination beam.
31. The method of claim 27, wherein said step (a) further comprises producing a custom polarized illumination beam.

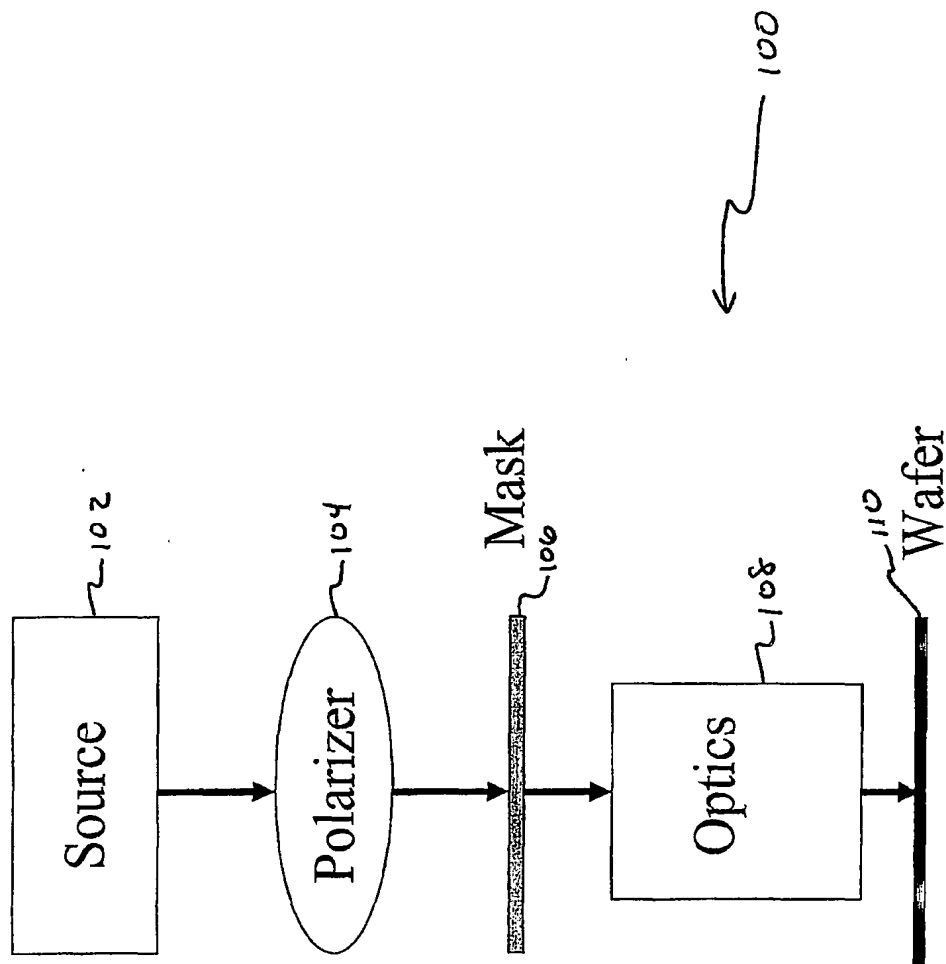


FIG. 1



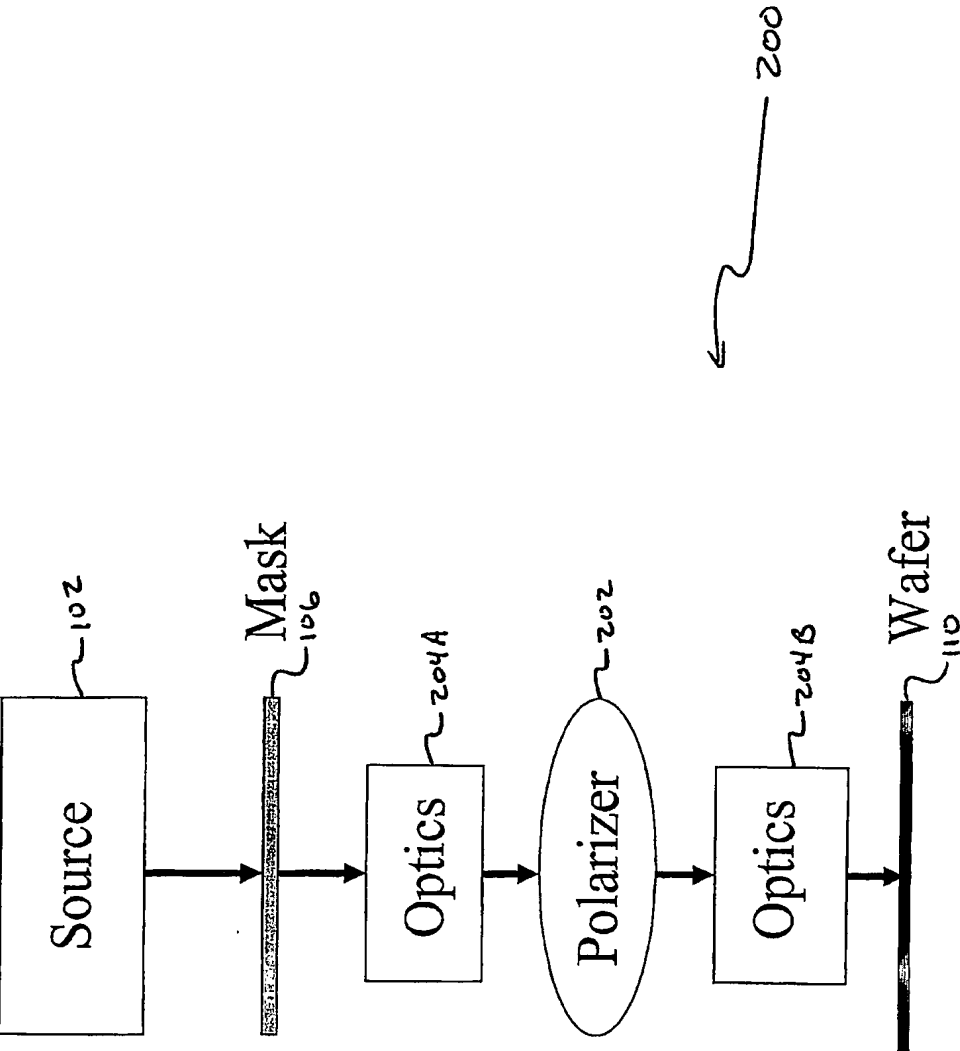


FIG. 2

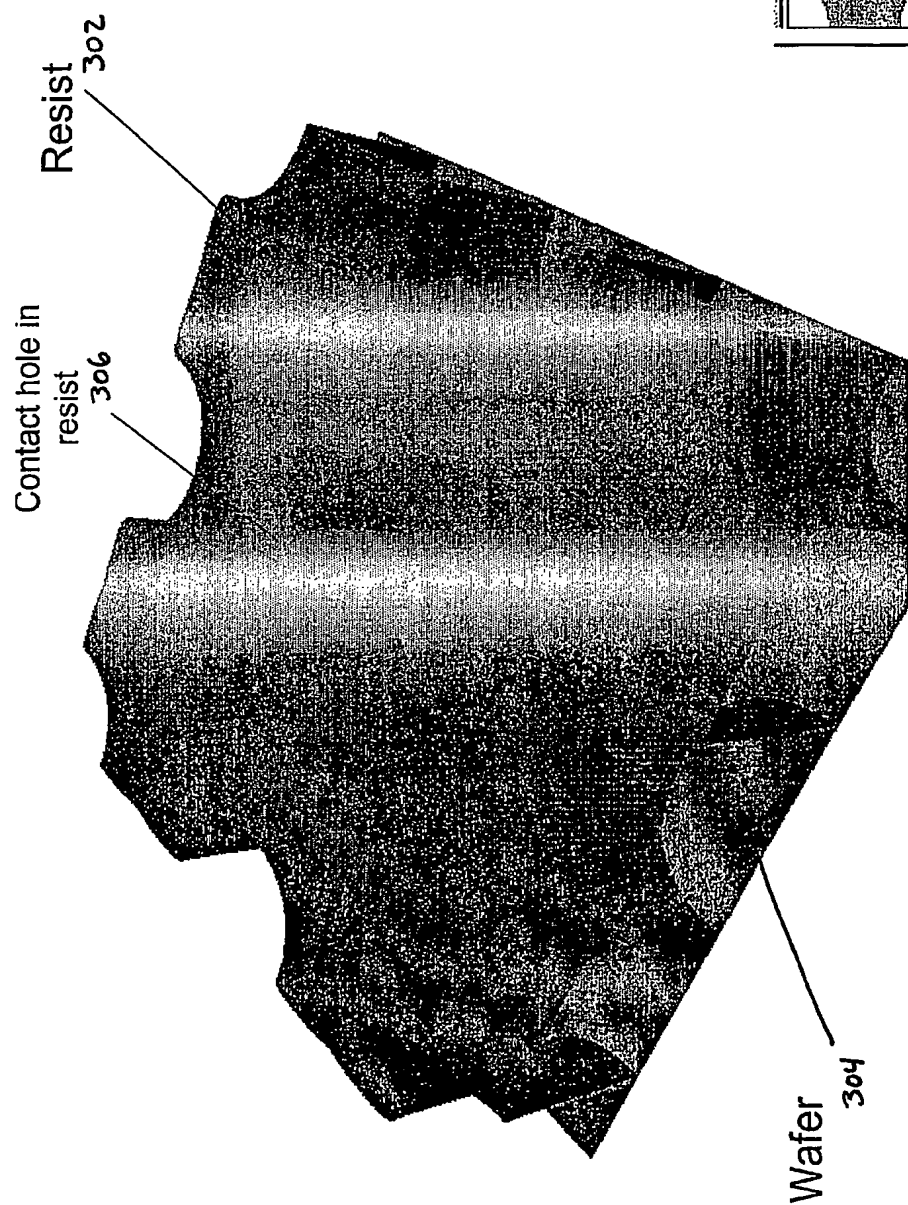


FIG. 3A

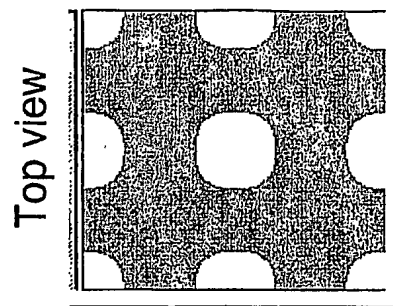


FIG. 3B

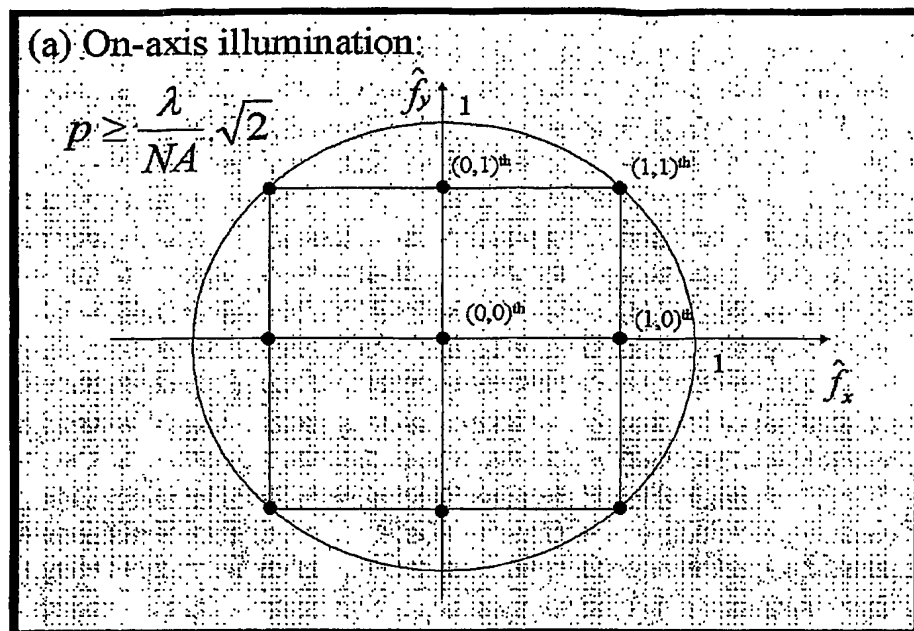


FIG. 4A

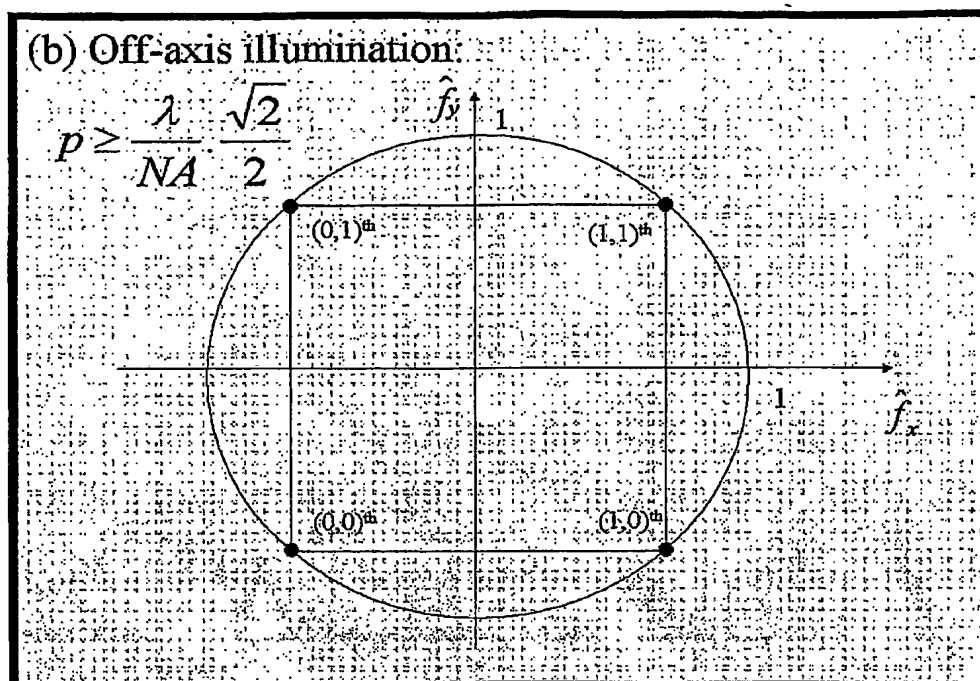


FIG. 4B

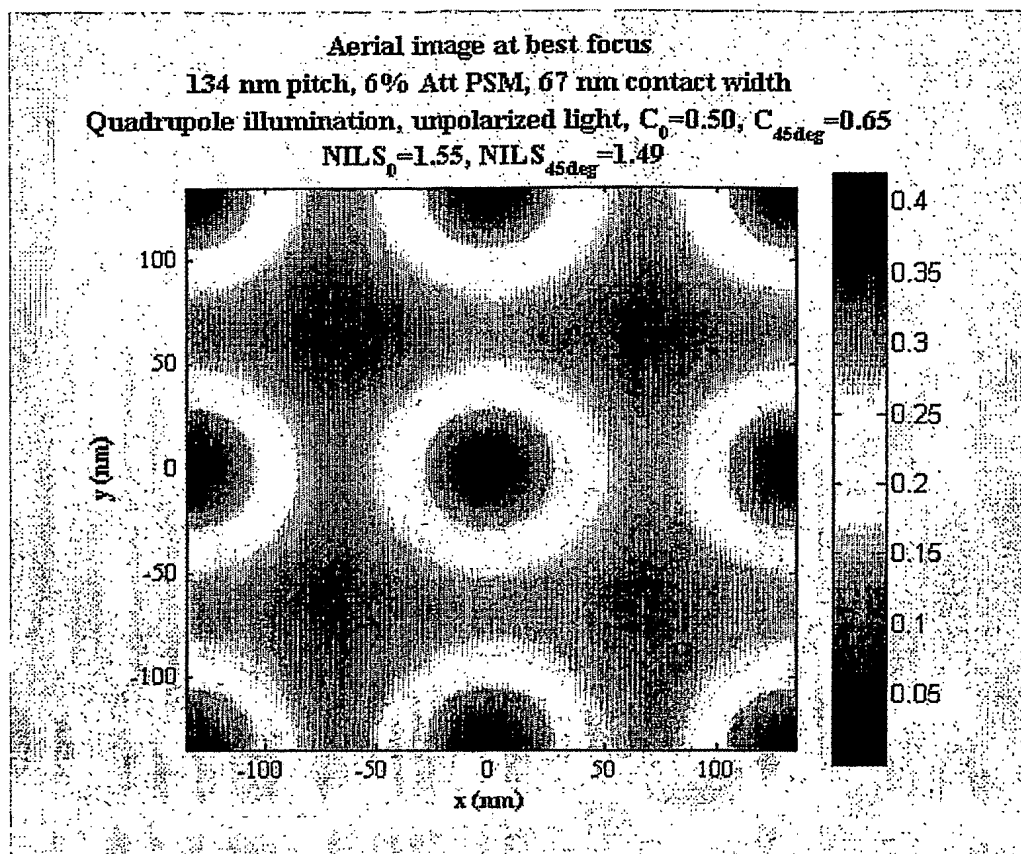


FIG. 5

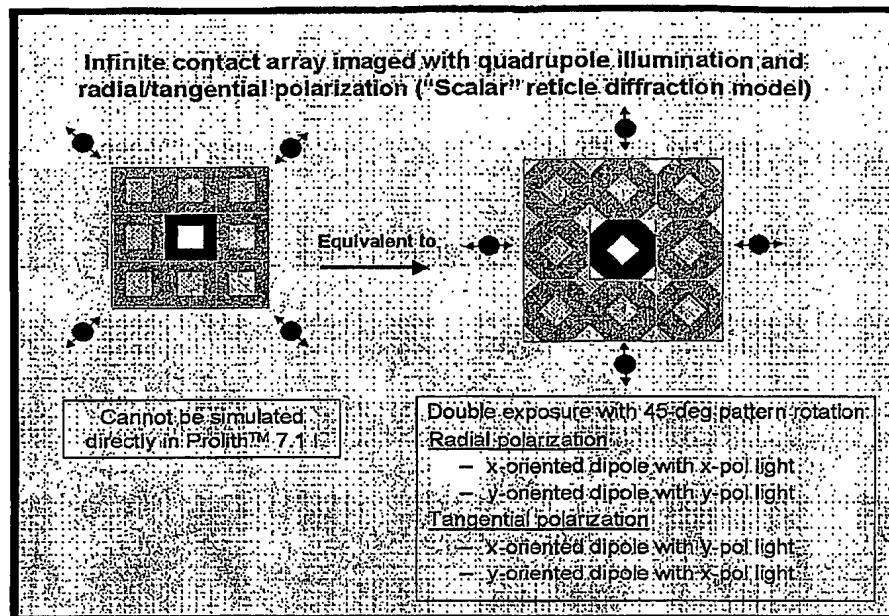


FIG. 6

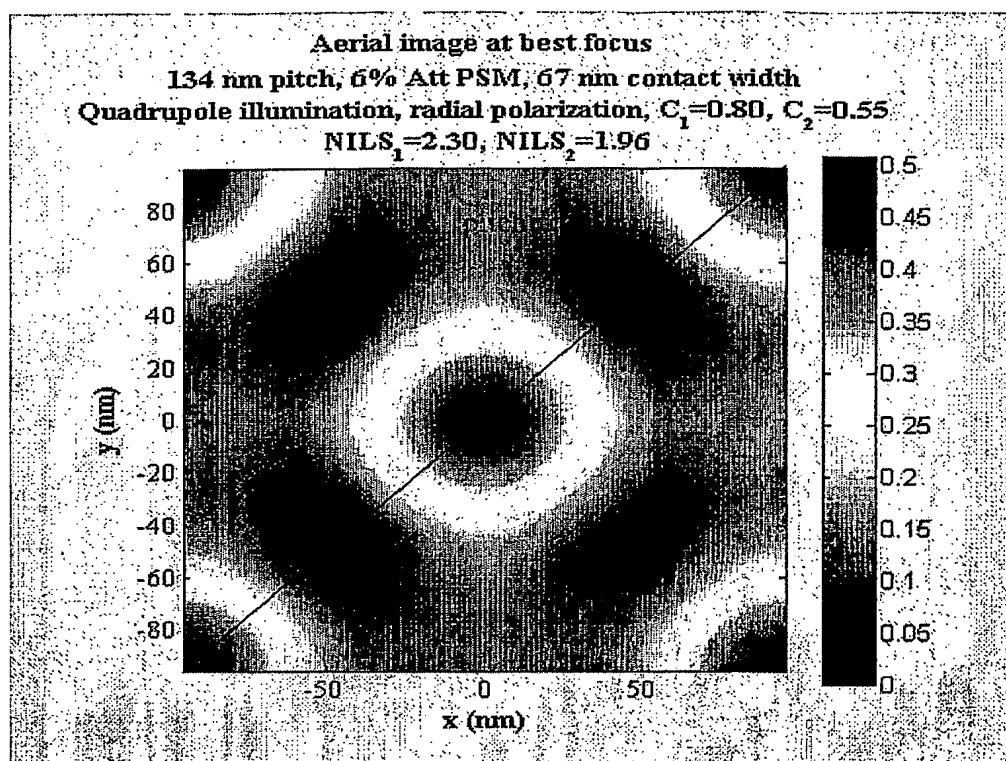


FIG. 7A

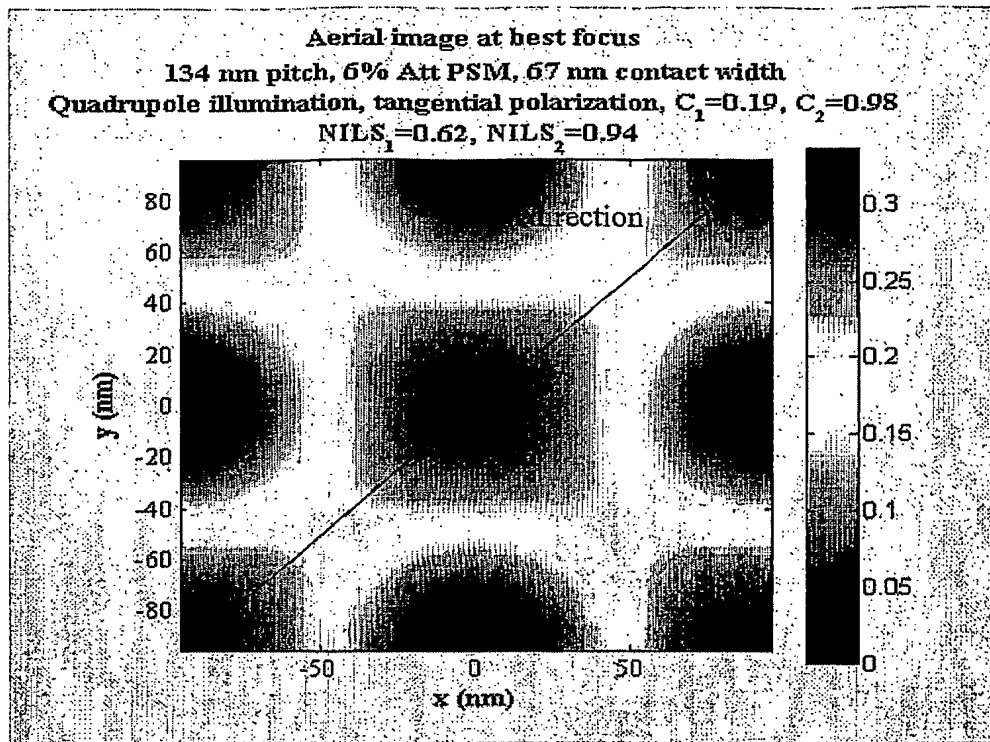


FIG. 7B



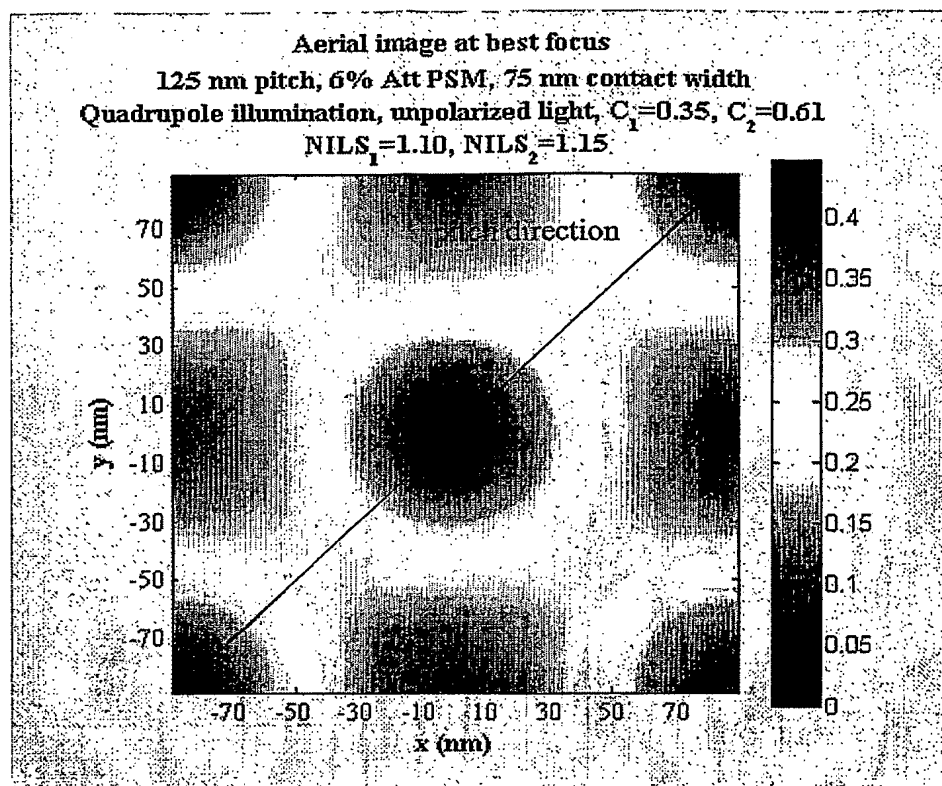


FIG. 8A

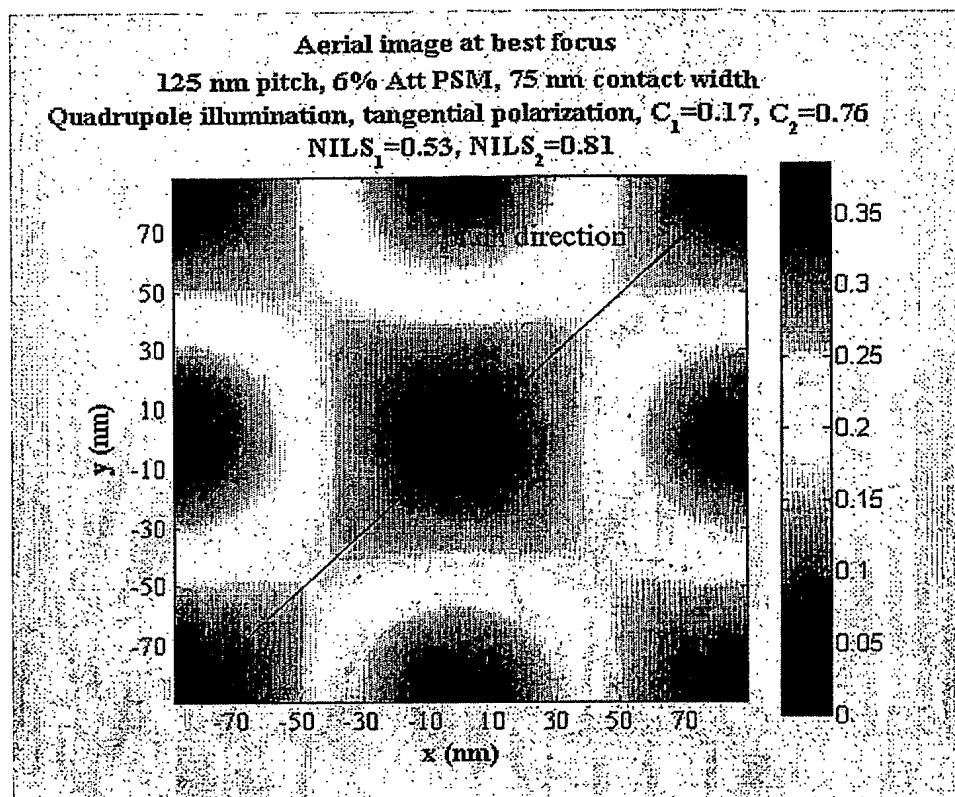


FIG. 8B

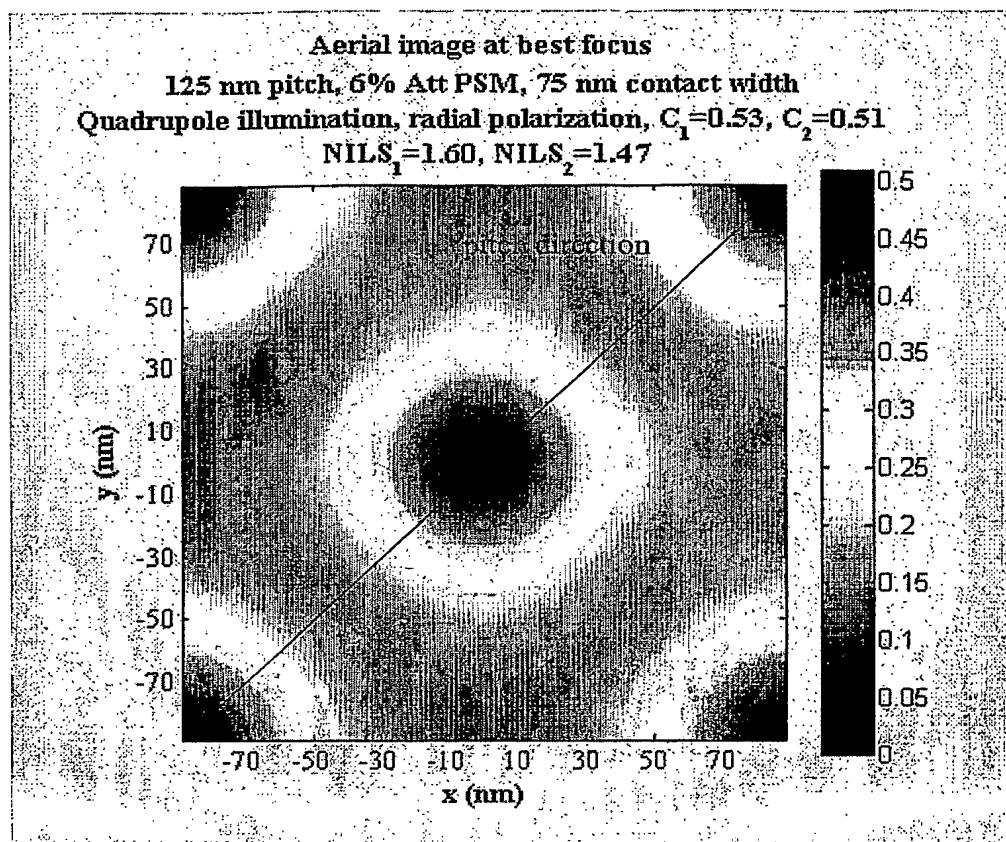


FIG. 8C

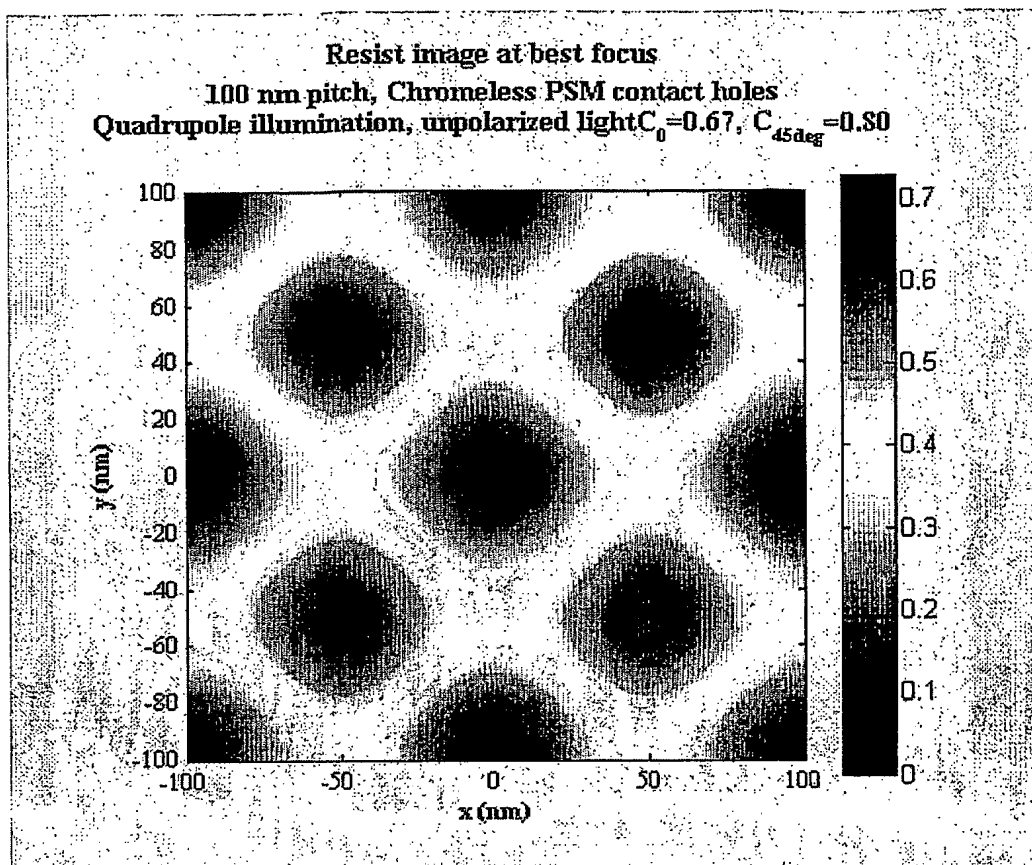


FIG. 9A

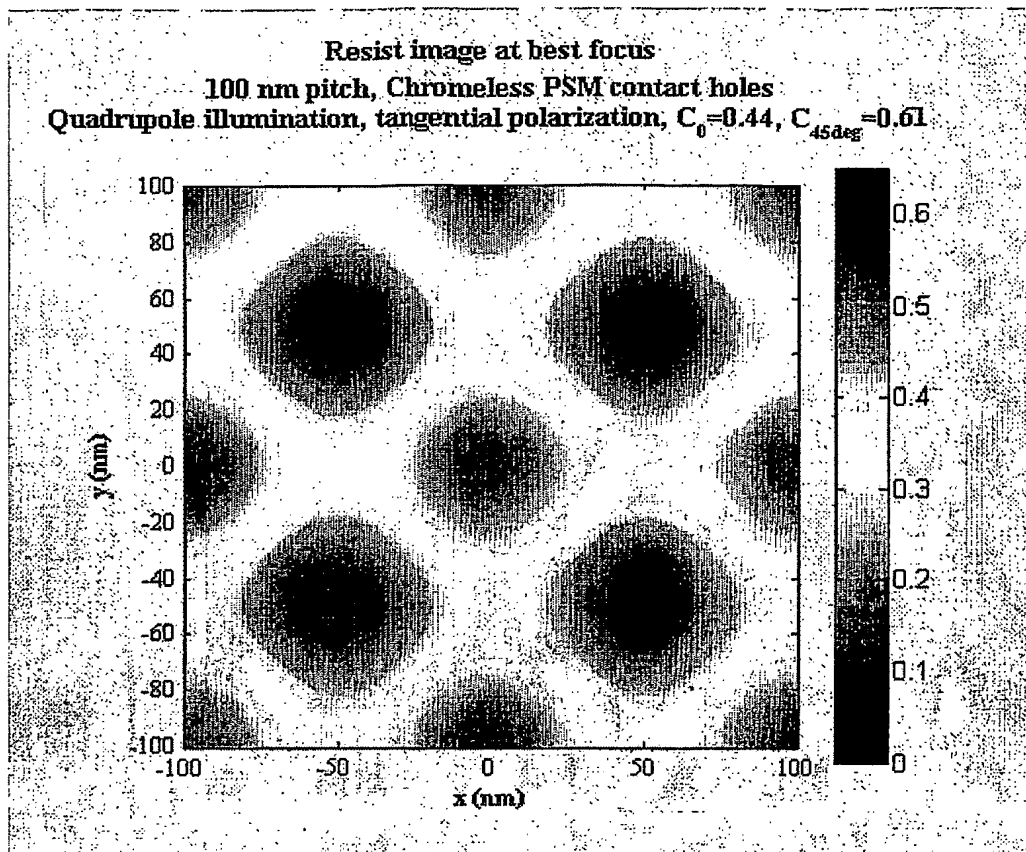


FIG. 9B

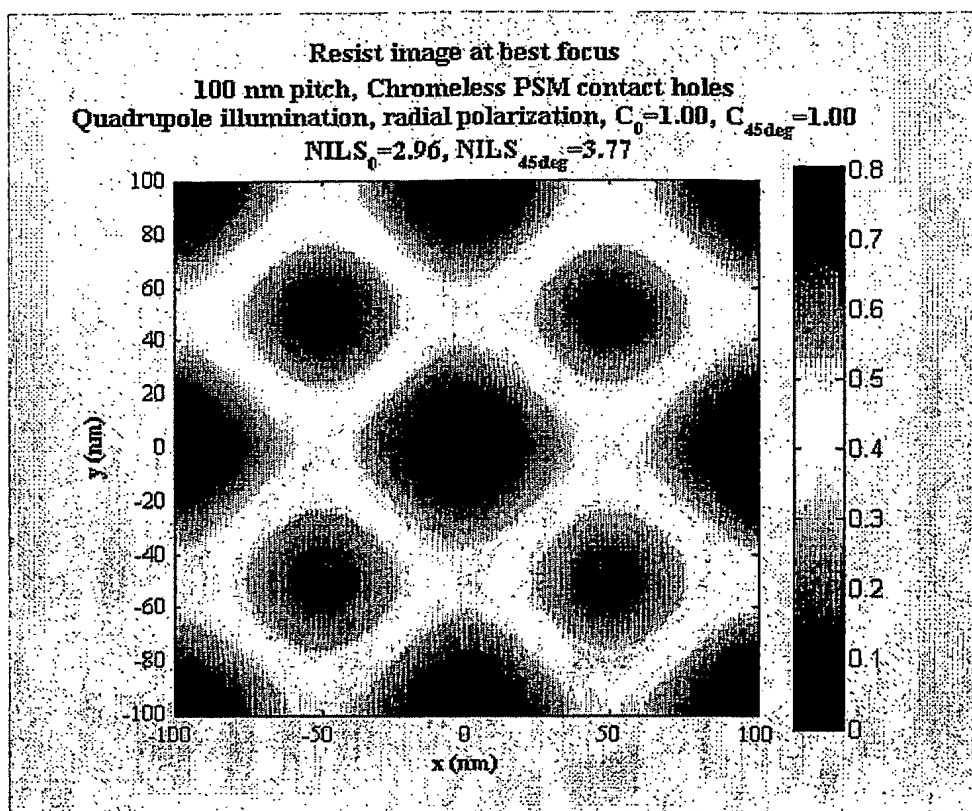


FIG. 9C

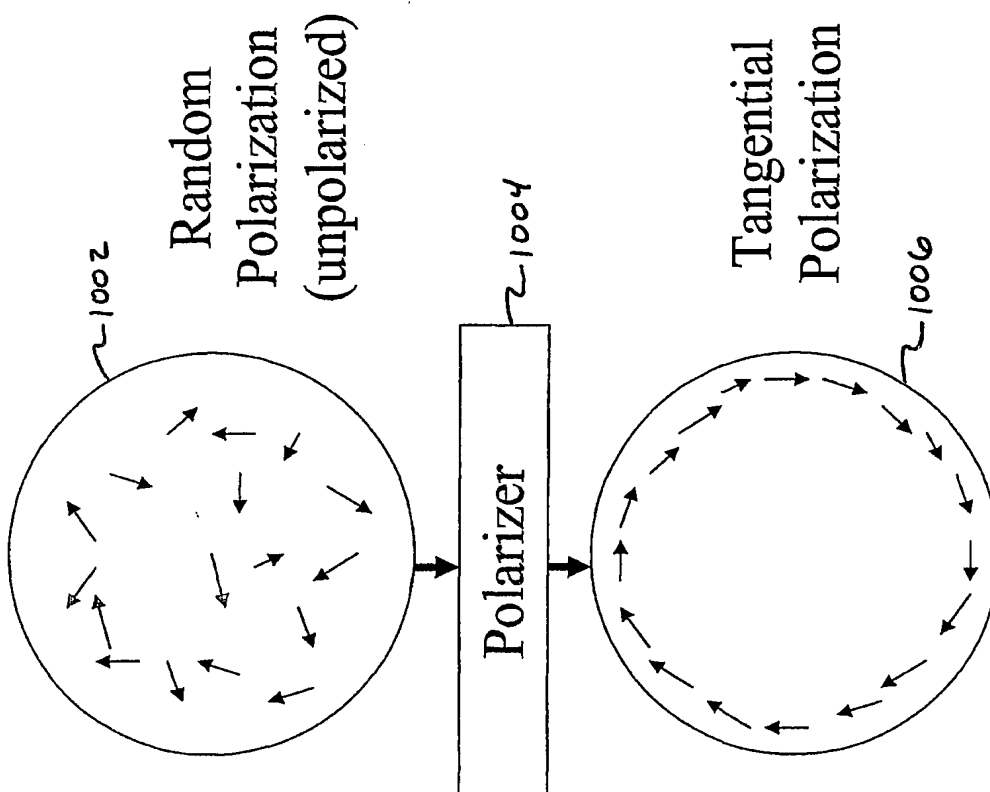


FIG. 10A

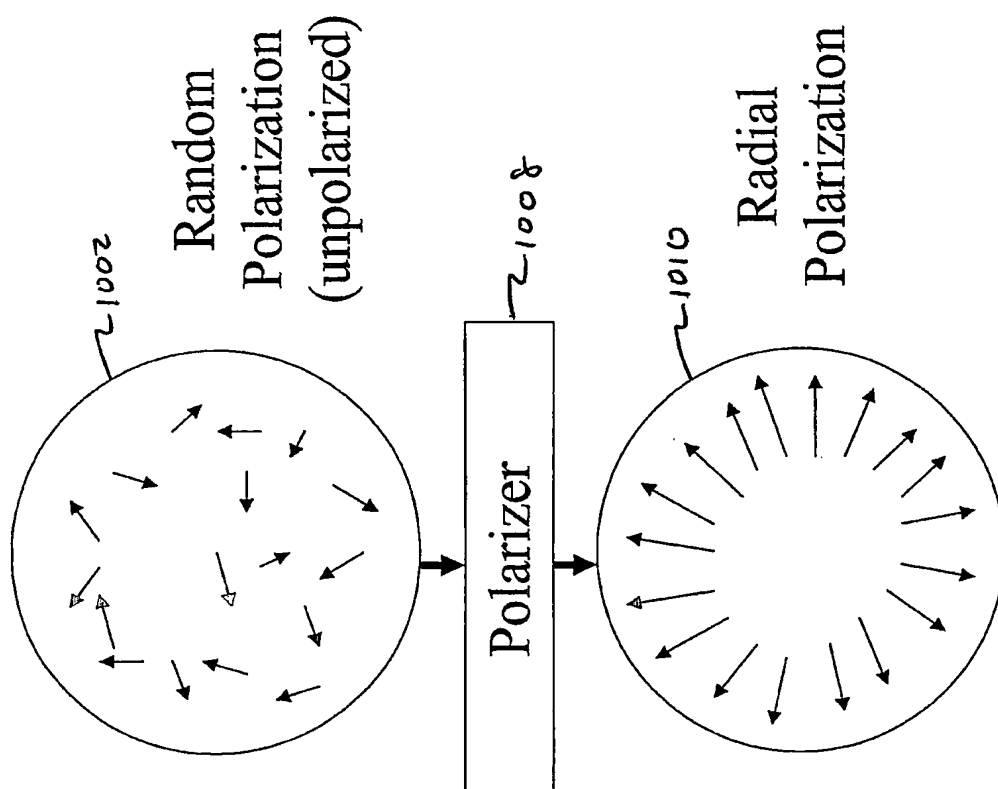


FIG. 10B



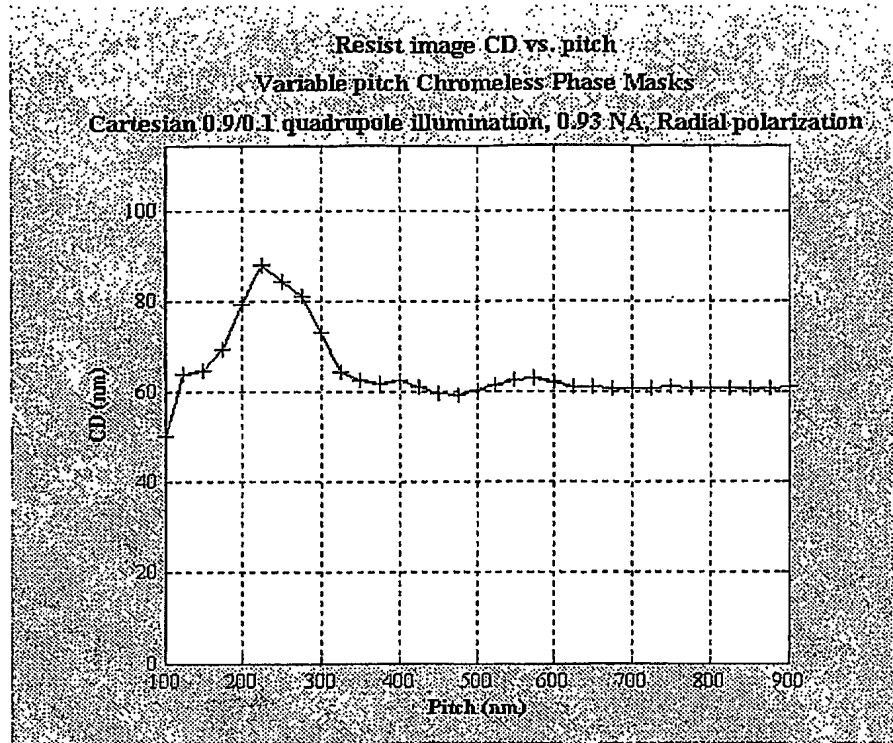
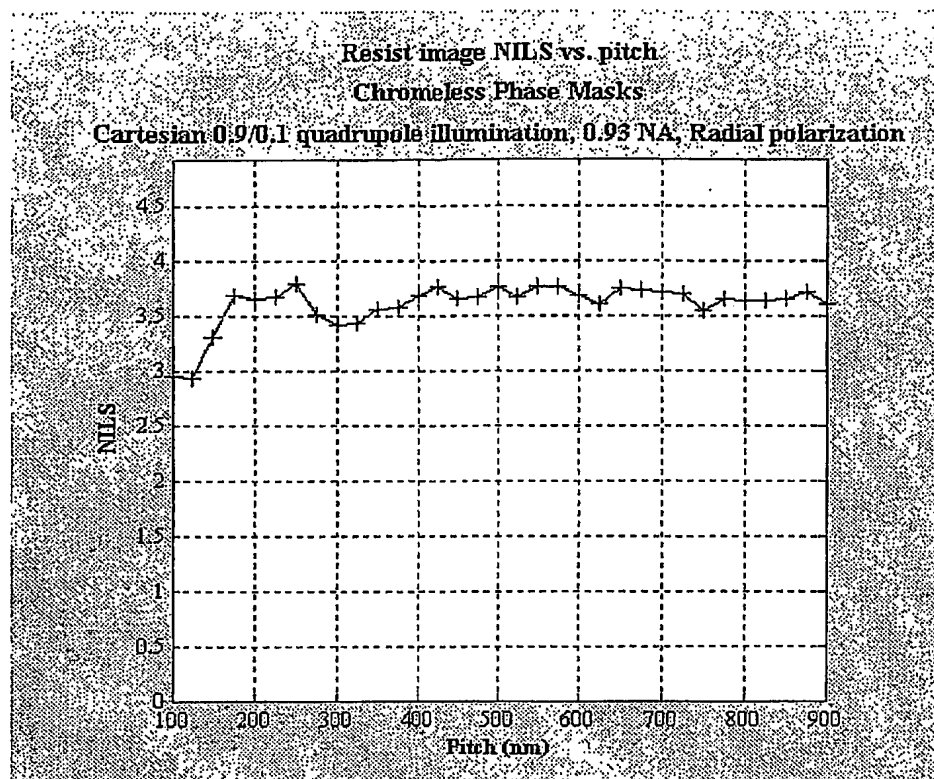


FIG. 11A

**FIG. 11B**

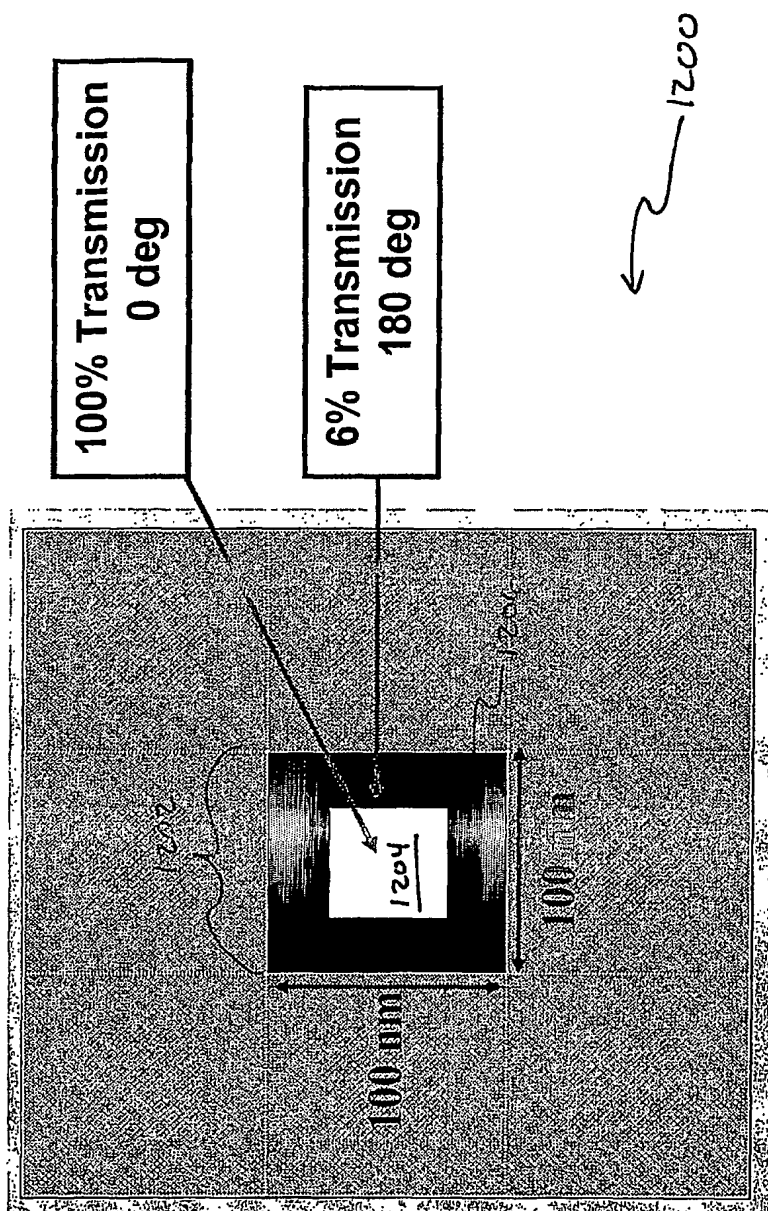


FIG. 12

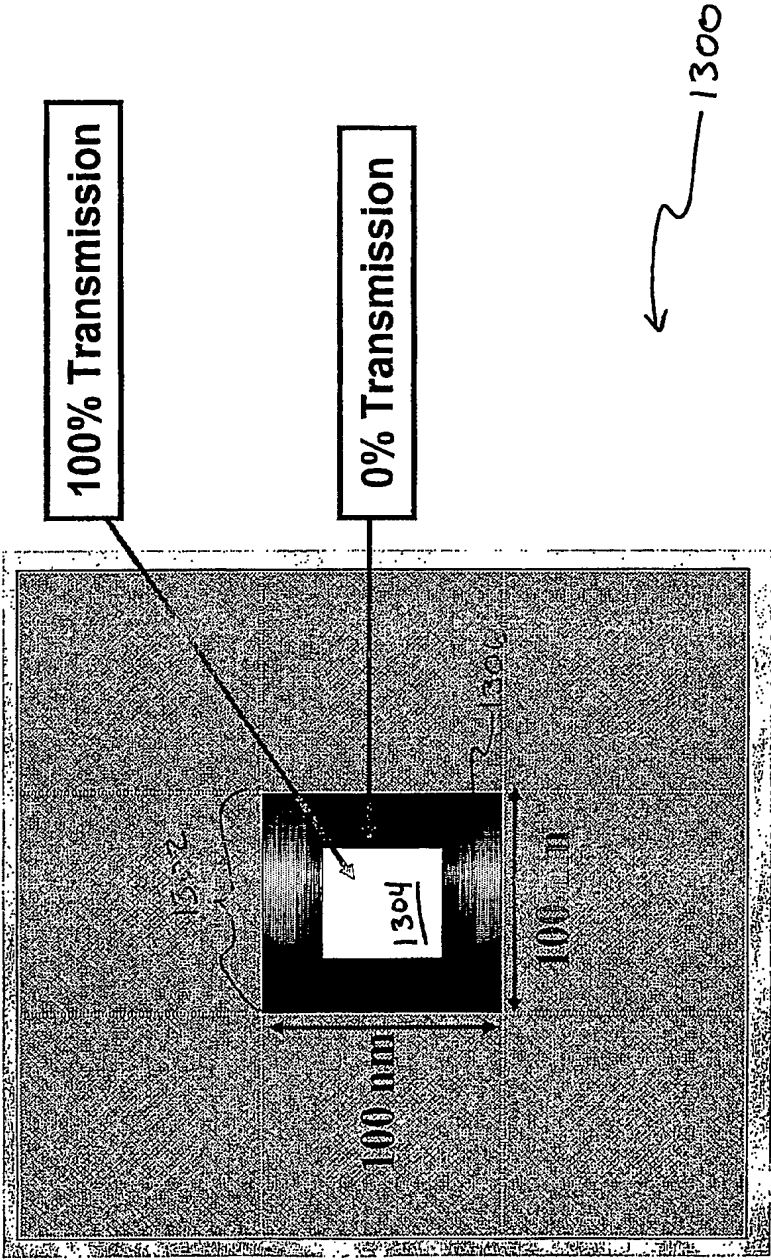


FIG. 13

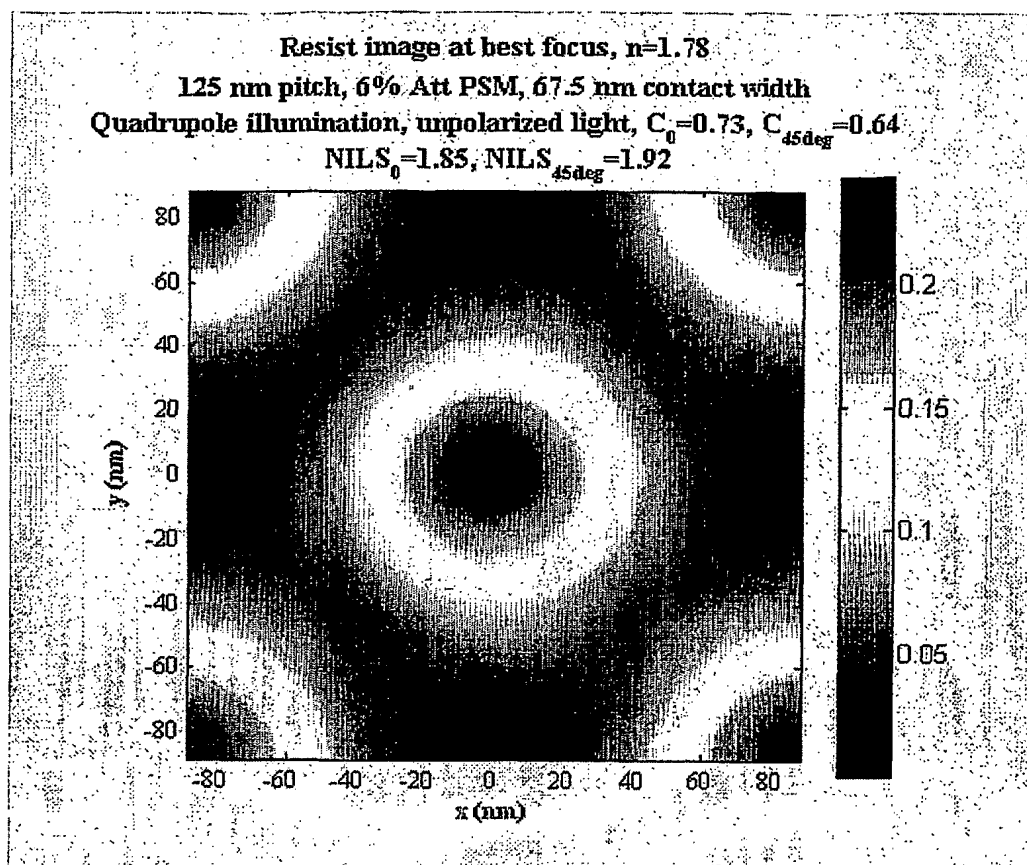


FIG. 14A

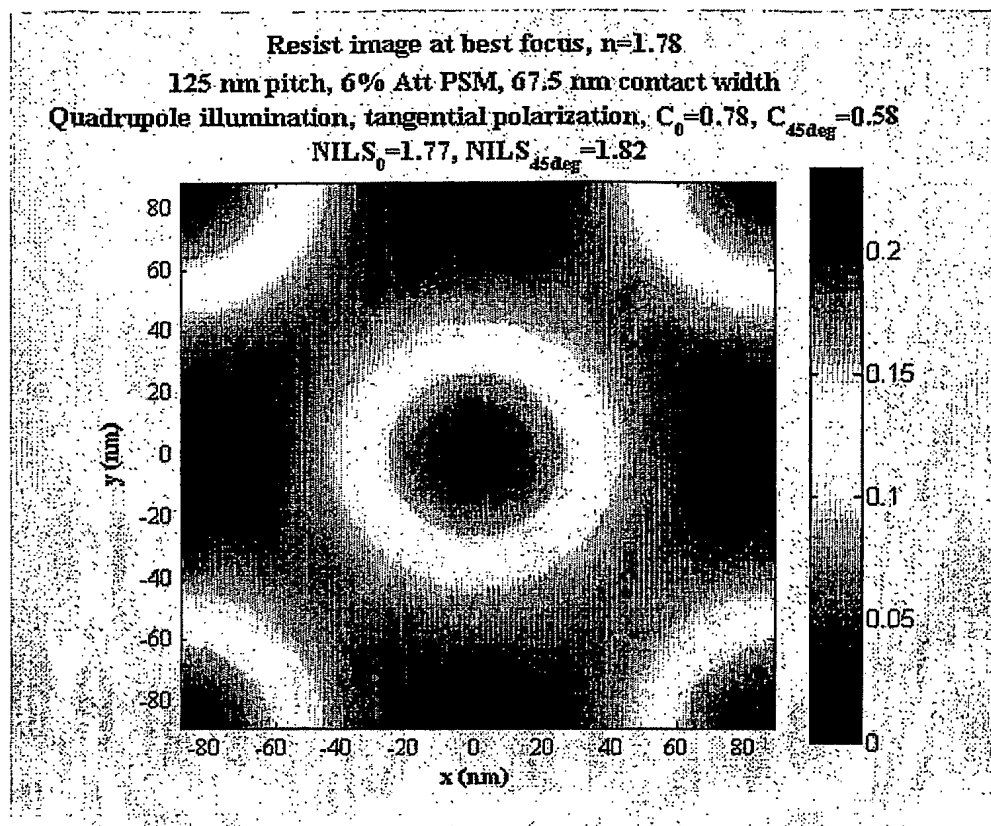


FIG. 14B

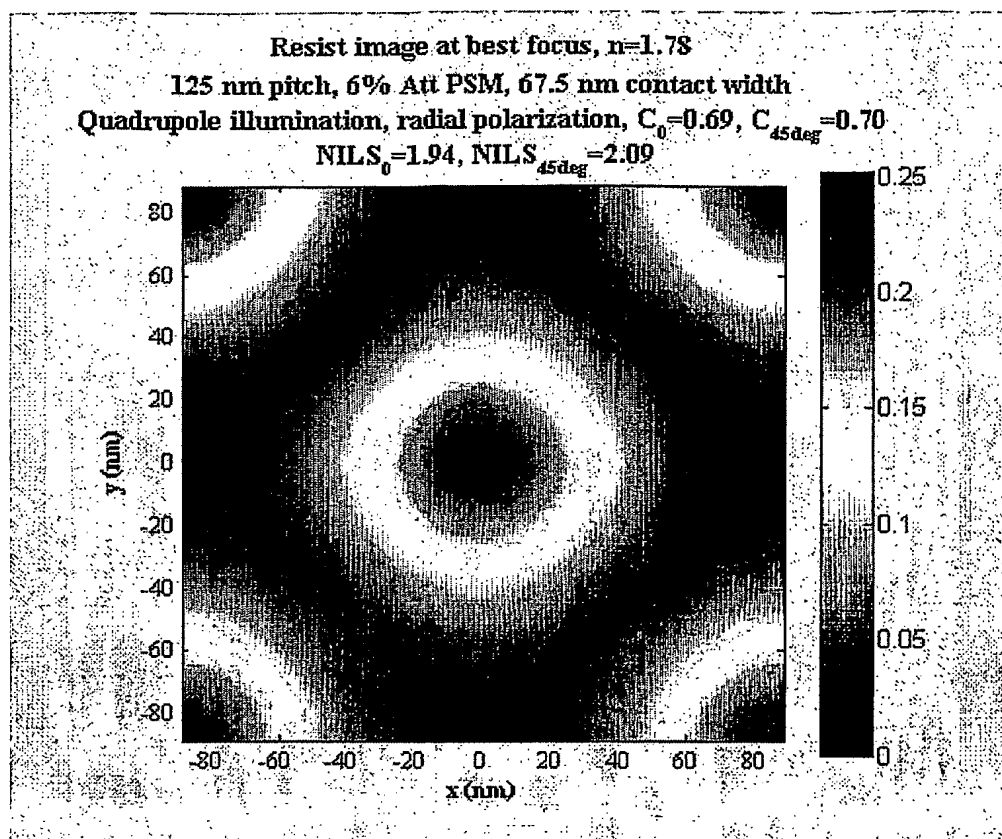


FIG. 14C

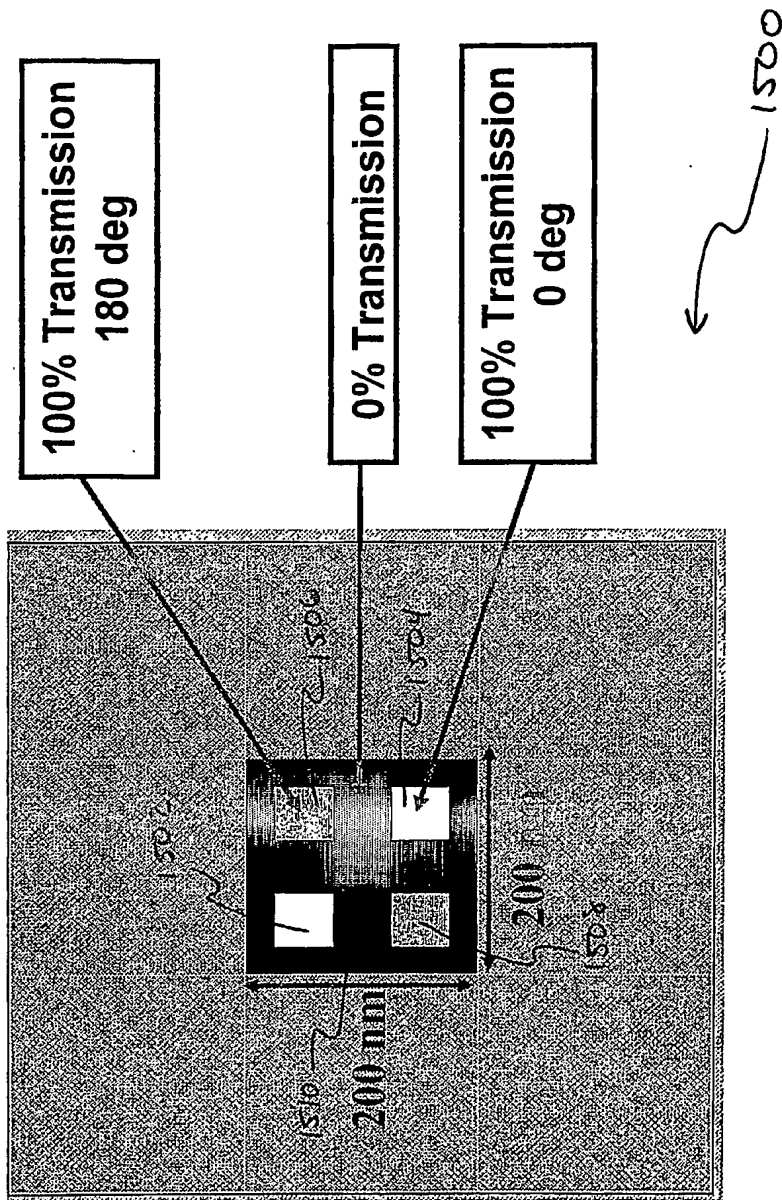
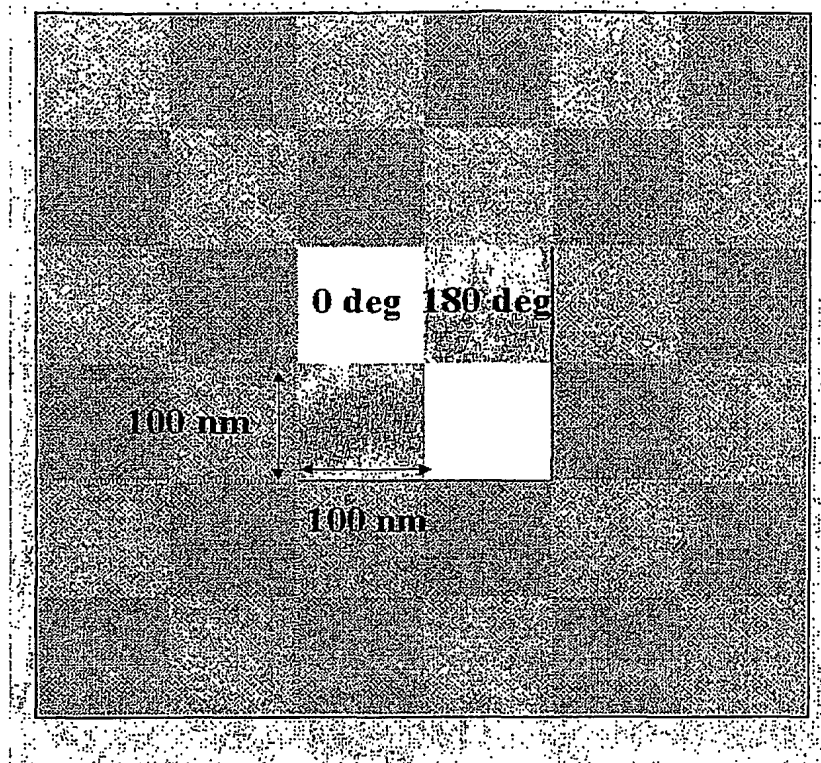


FIG. 15





**FIG. 16**

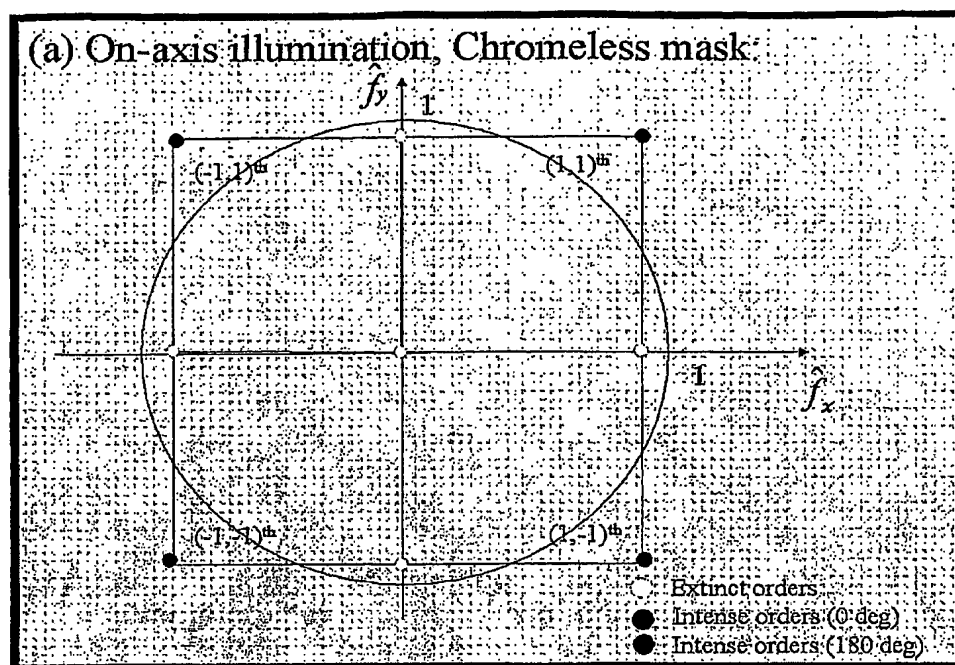


FIG. 17A

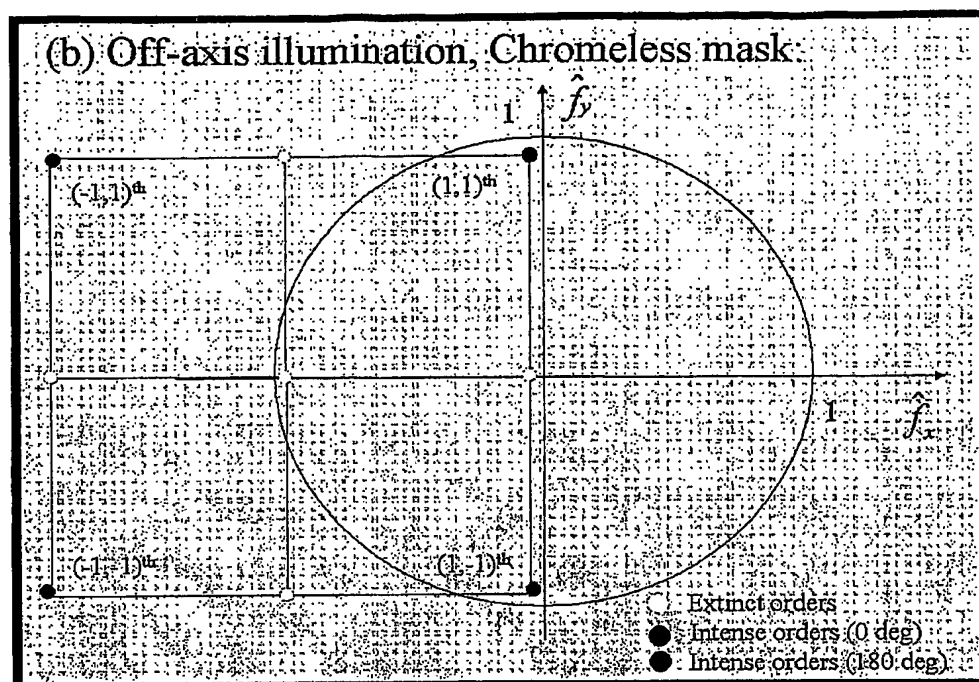


FIG. 17B

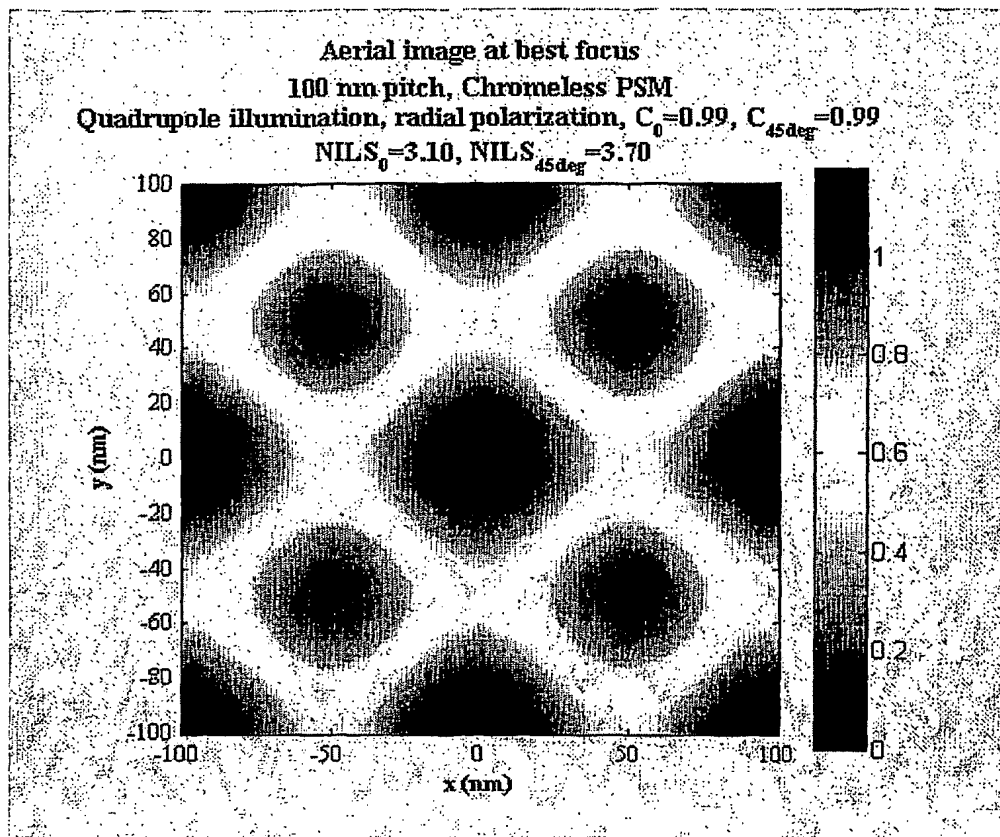
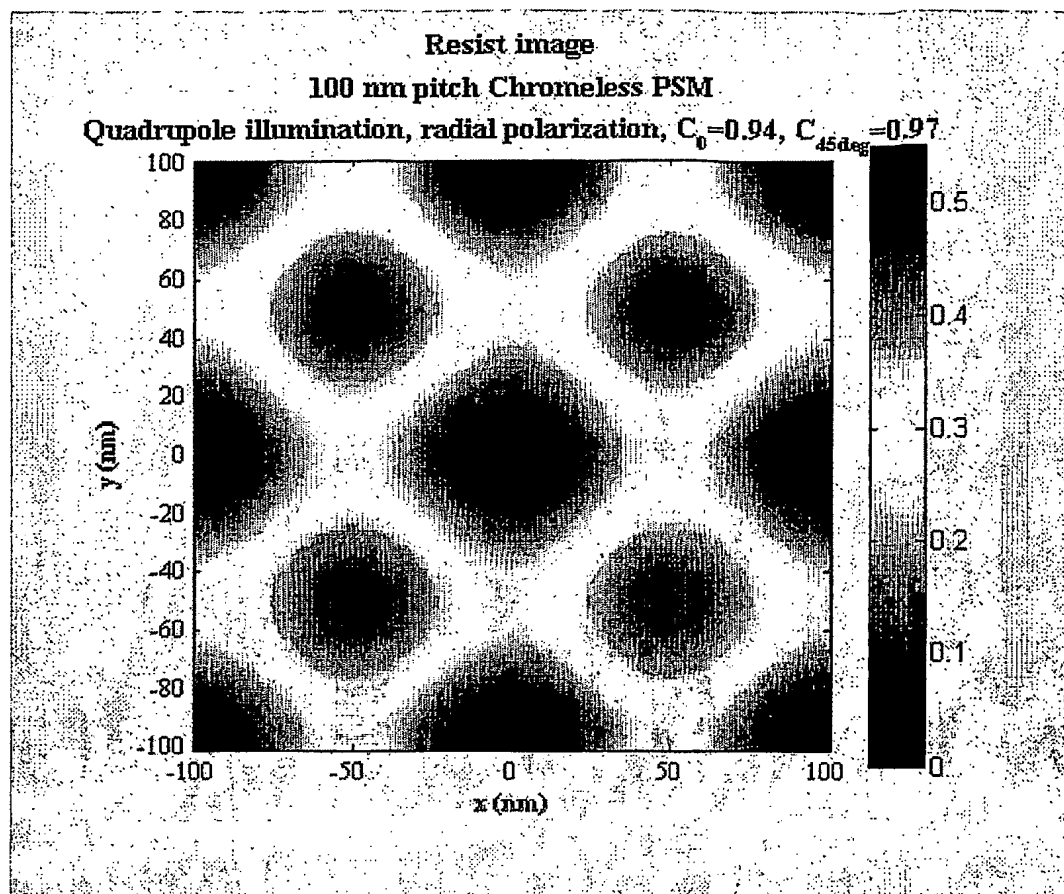


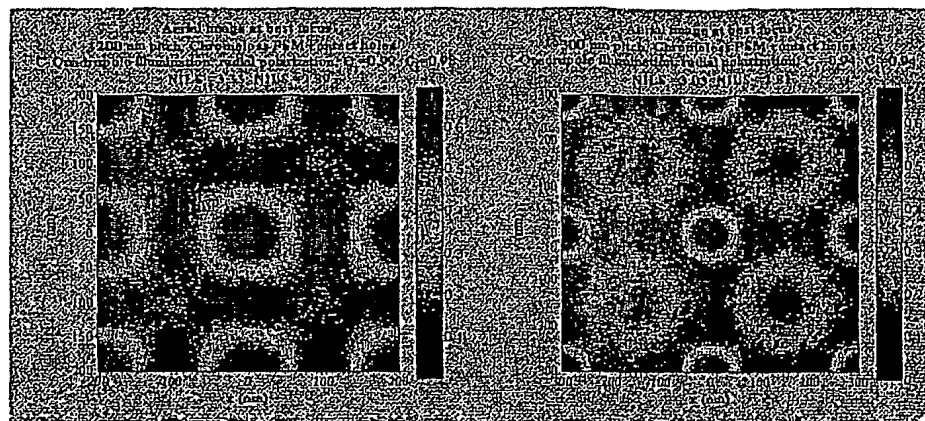
FIG. 18A

**FIG. 18B**

Aerial image at best focus, variable pitch, chrome,  
alternating PSMs

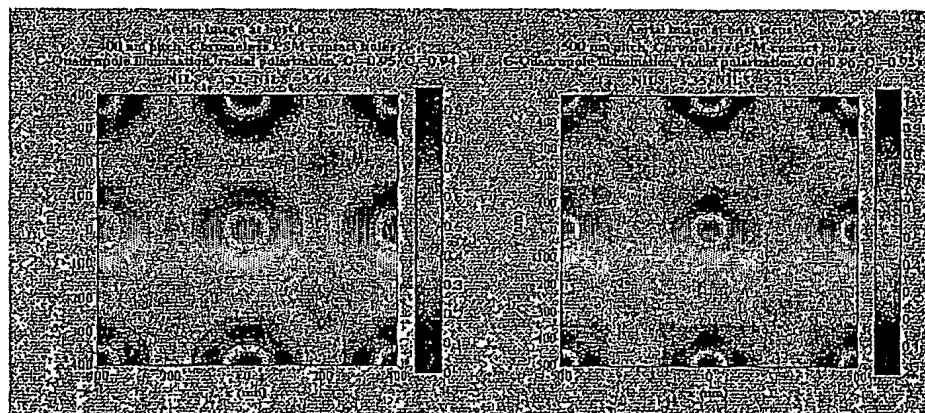
200-nm pitch

300-nm pitch



400-nm pitch

500-nm pitch



600-nm pitch

1000-nm pitch

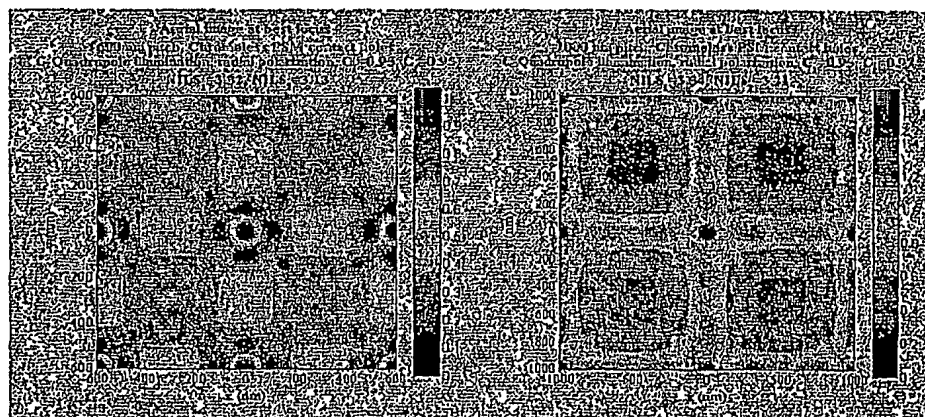
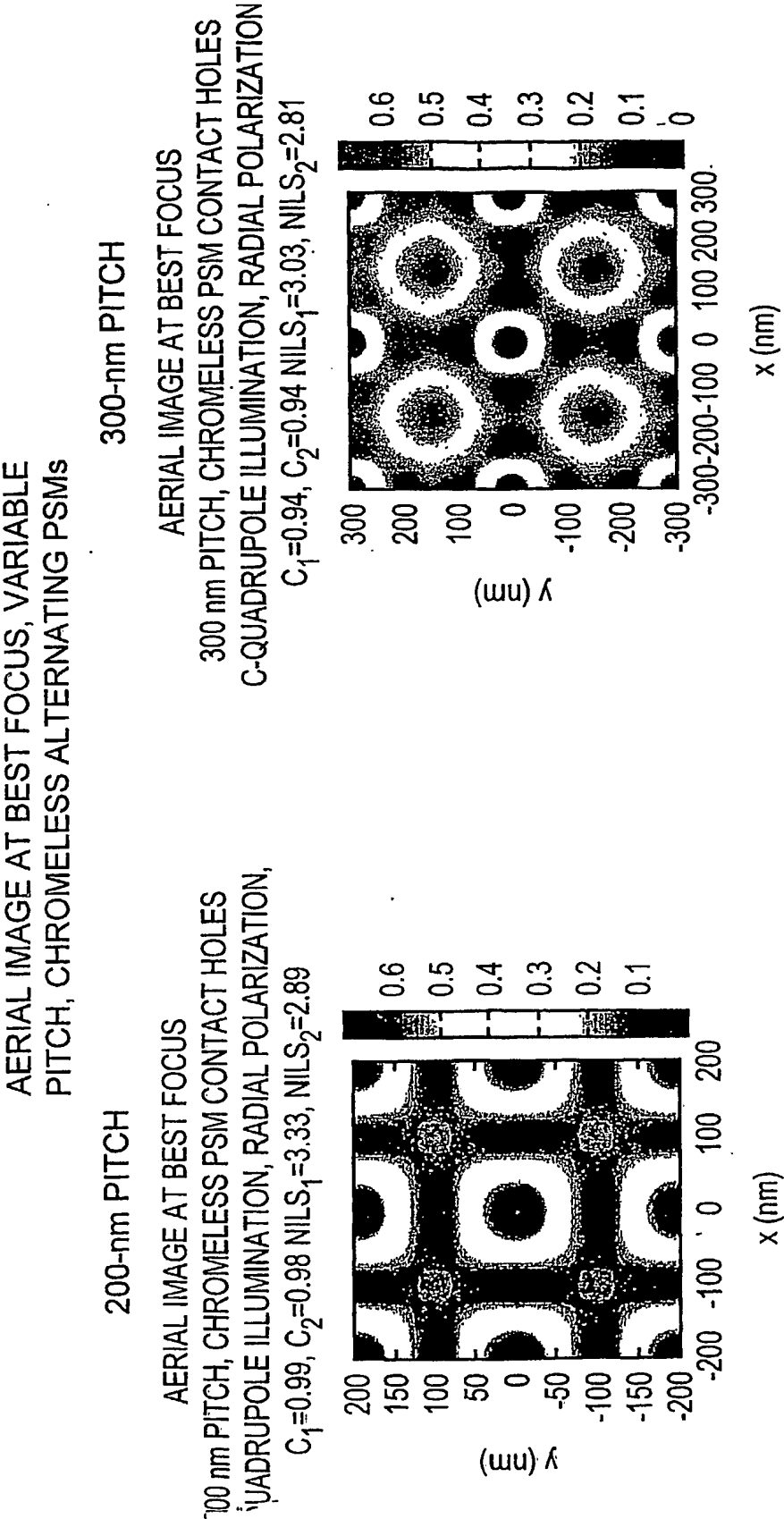


FIG. 19



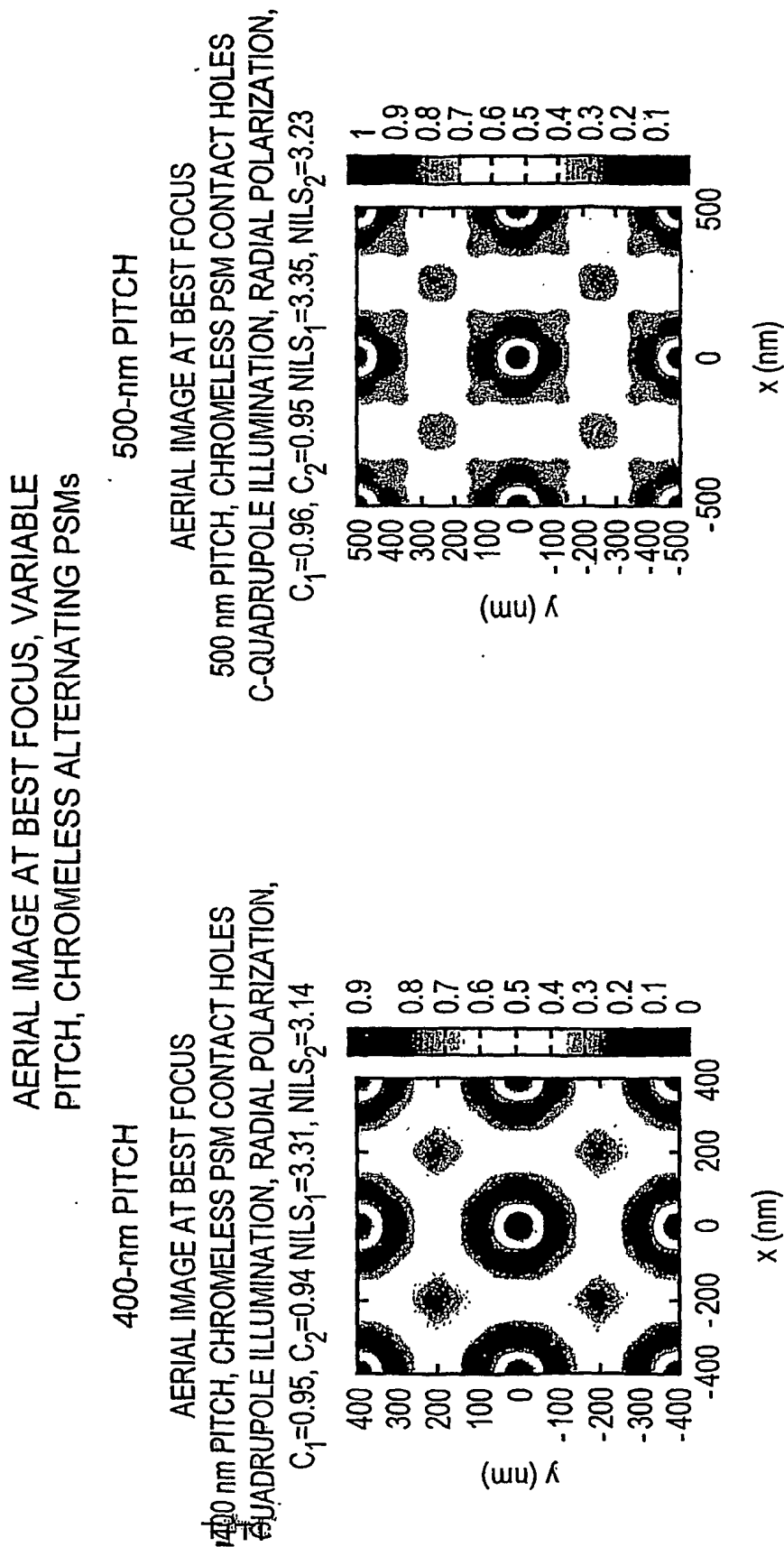


FIG.19B



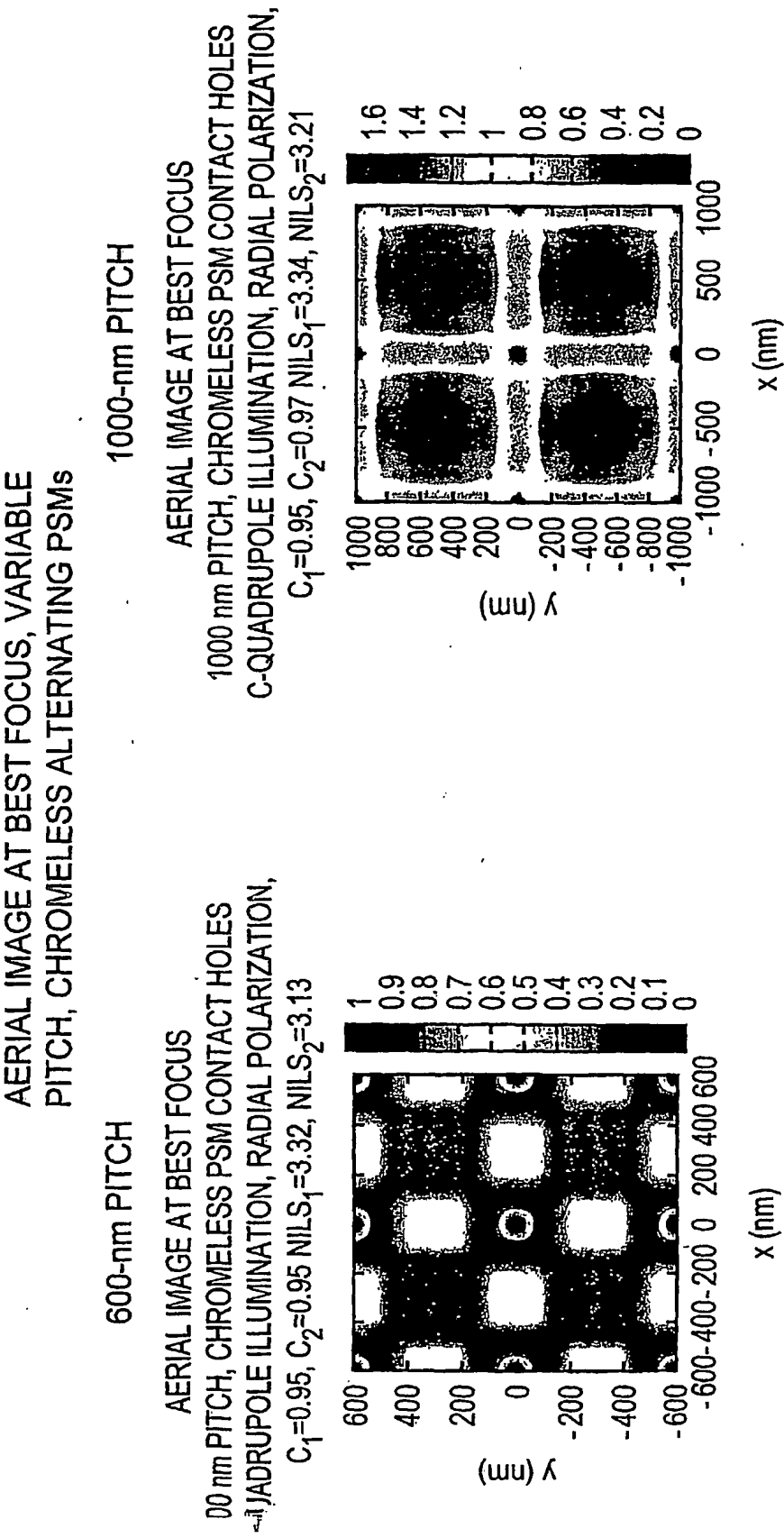


FIG.19C

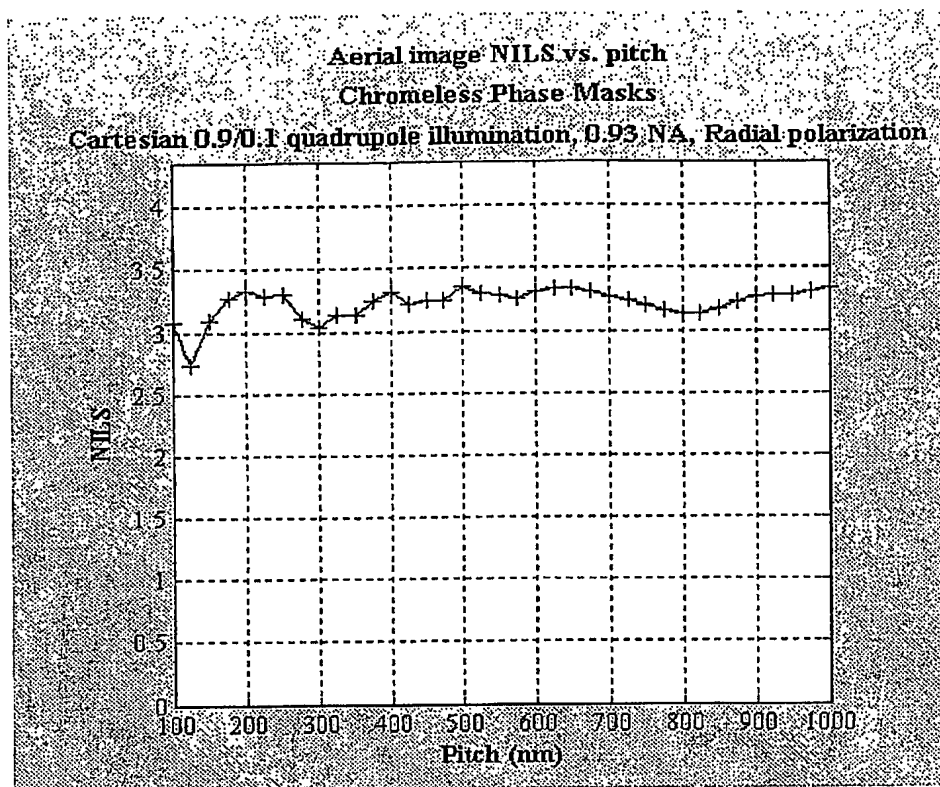
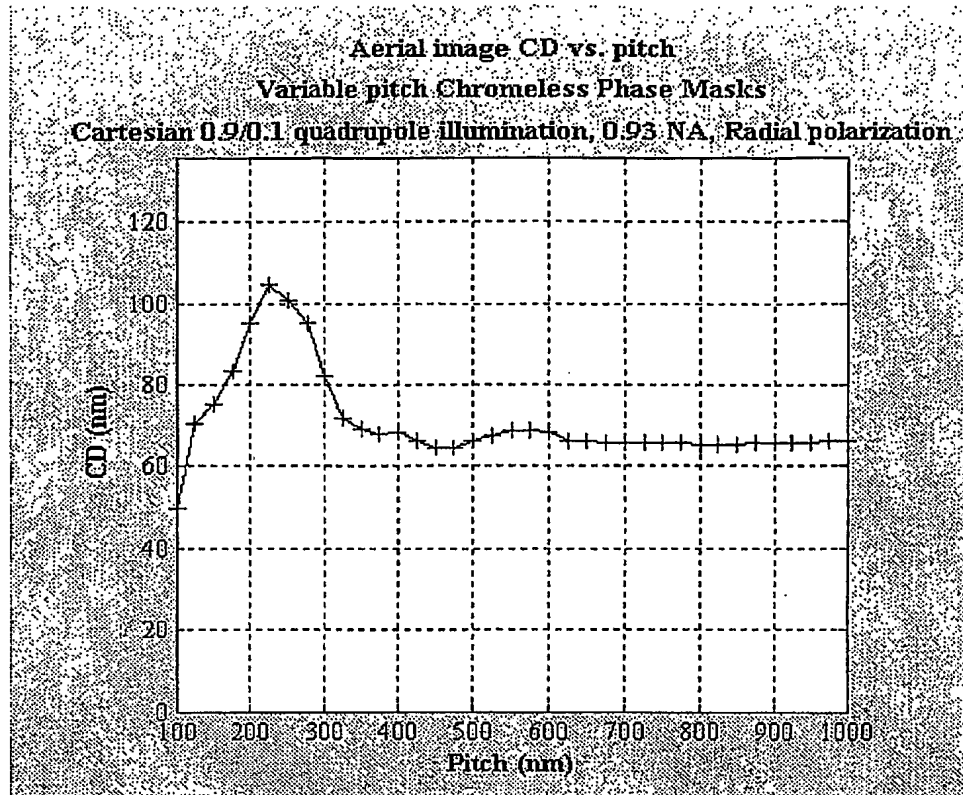


FIG. 20A

**FIG. 20B**

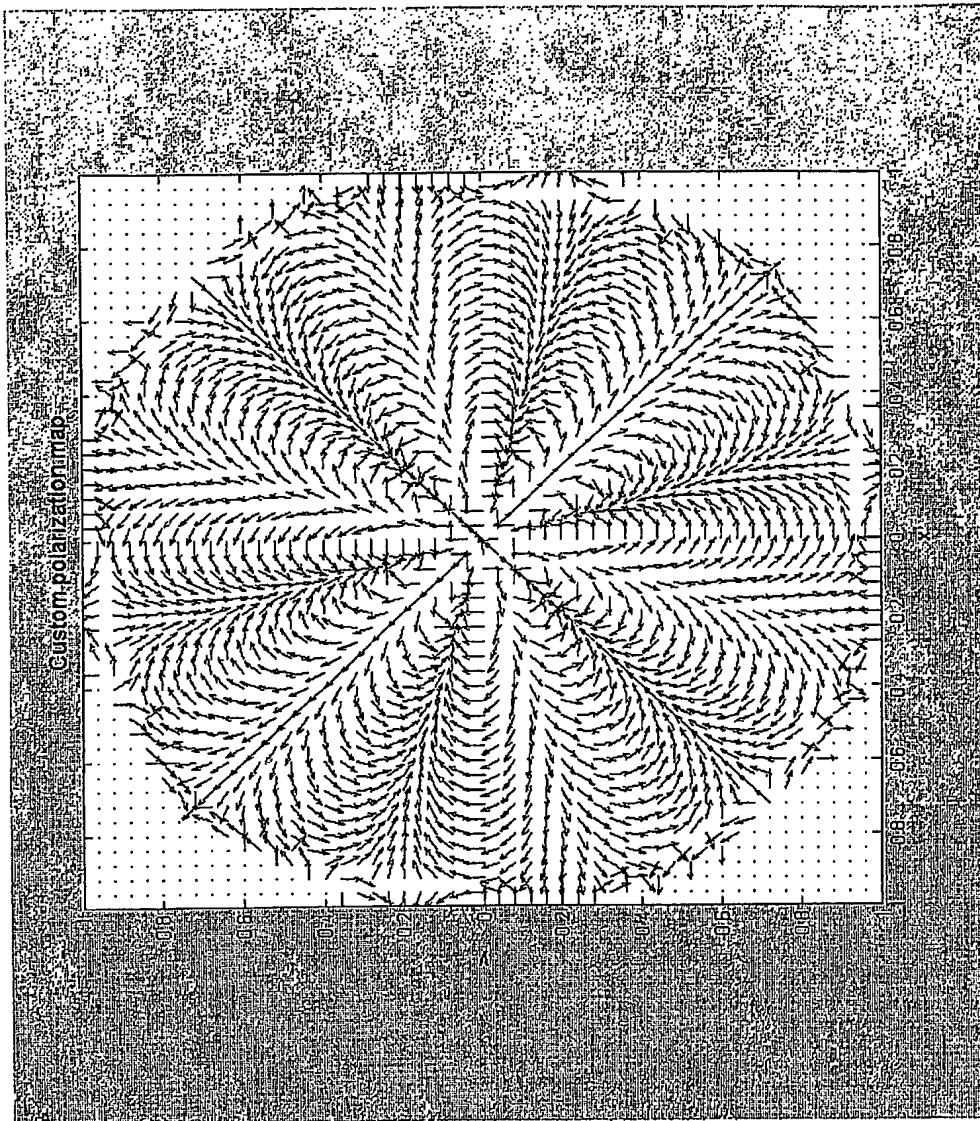


FIG. 21A

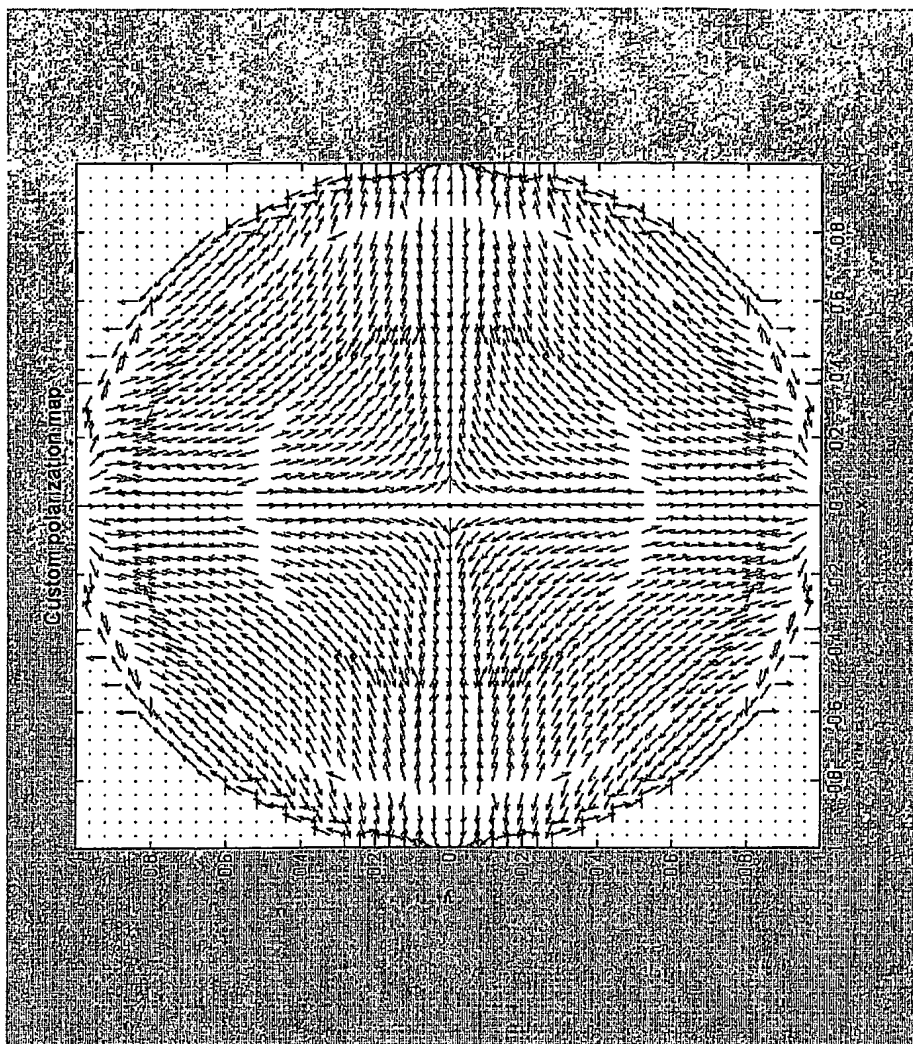


FIG. 21B

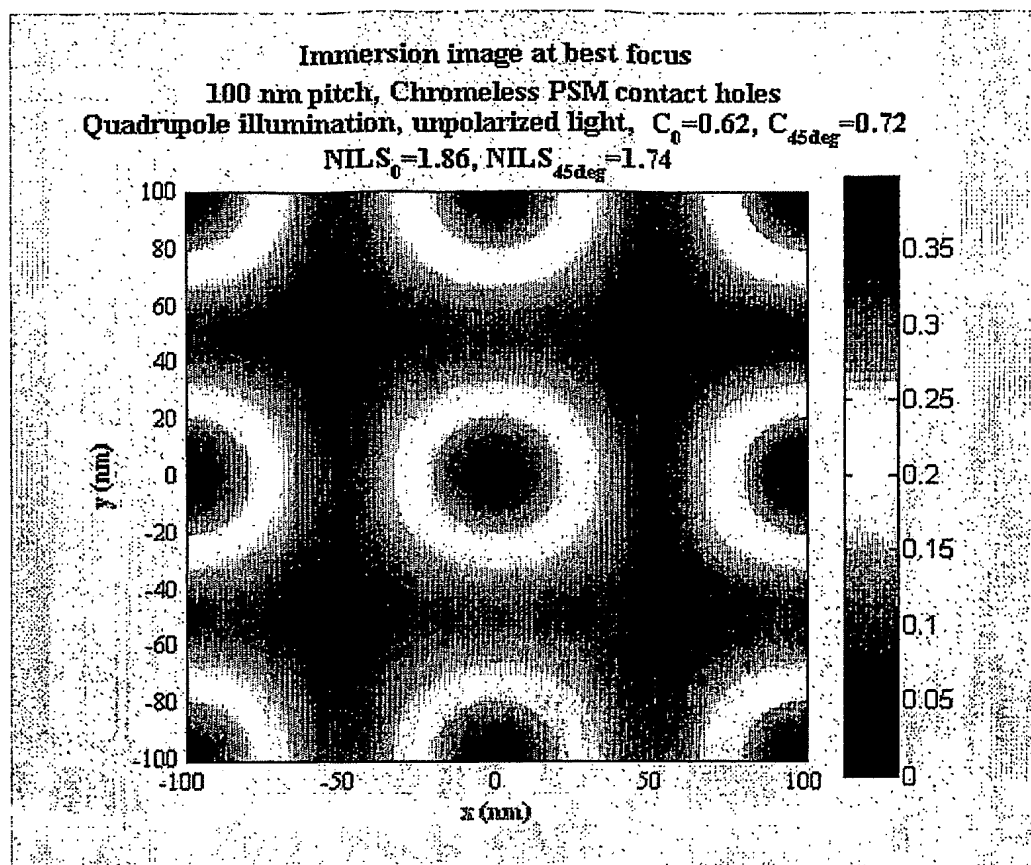


FIG. 22

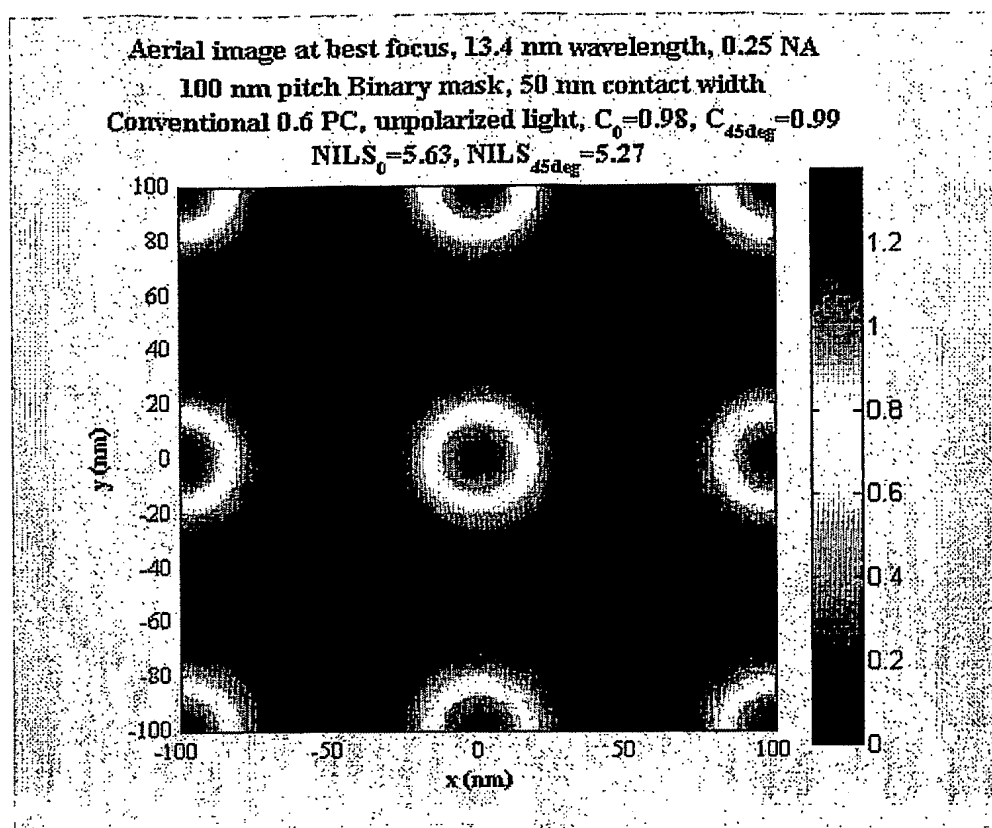


FIG. 23

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(54) Title: LITHOGRAPHIC PRINTING WITH POLARIZED LIGHT

(57) Abstract: The present invention provides systems and methods for improved lithographic printing with polarized light. In embodiments of the present invention, polarized light (radially or tangentially polarized) is used to illuminate a phase-shift mask (PSM) and produce an exposure beam. A negative photoresist layer is then exposed by light in the exposure beam. A chromeless PSM can be used. In further embodiments of the present invention, radially polarized light is used to illuminate a mask and produce an exposure beam. A positive photoresist layer is then exposed by light in the exposure beam. The mask can be an attenuating PSM or binary mask. A very high image quality is obtained even when printing contact holes at various pitches in low k applications.

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
Please See Continuation Sheet

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,541,026 (MATSUMOTO) 30 July 1996 (30.07.1996), column 2, lines 60-67, column 3, lines 1-64, and col 8, lines 1-21.	1-4, 6-7, 9-15, 17-19, 21-31
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Y		5, 8, 16, 20
Y	US 2002/0176166 A1 (SCHUSTER) 28 November 2002 (28.11.2002), paragraph [0053].	5
Y	US 5,539,514 (SHISHIDO et al) 23 July, 1996 (23.07.1996), column 29, lines 19-21.	8, 20
Y	US 5,467,166 (SHIRAISHI) 14 November 1995 (14.11.1995), column 14, lines 11-37.	16

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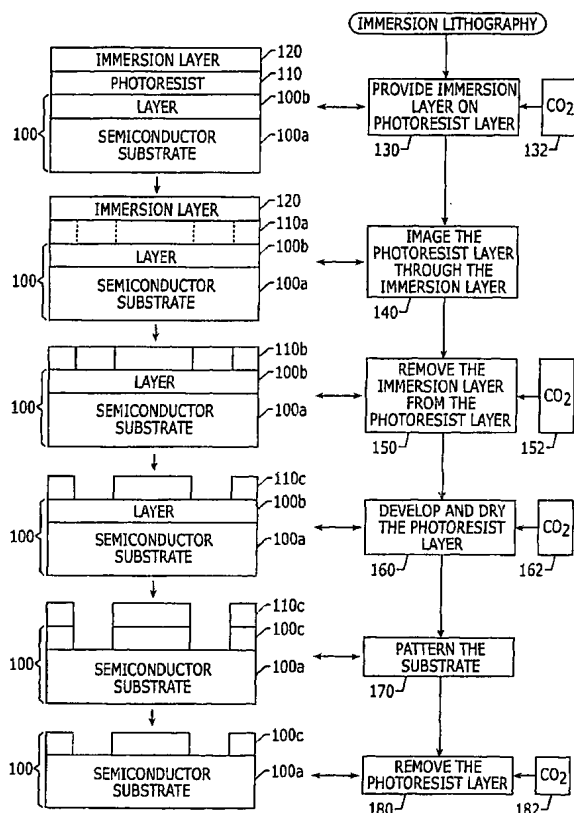
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(54) Title: **IMMERSION LITHOGRAPHY METHODS USING CARBON DIOXIDE**



(57) Abstract: A substrate is patterned by performing immersion lithography on a photoresist layer on the substrate using carbon dioxide. The immersion layer may be provided and/or removed and/or the photoresist layer may be developed, dried and/or removed using carbon dioxide. The immersion layer can include liquid and/or solid immersion layers. The need for organic solvents in immersion lithography can thereby be reduced or eliminated.

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## IMMERSION LITHOGRAPHY METHODS USING CARBON DIOXIDE

### Field Of The Invention

The present invention relates to methods of patterning a photoresist layer on a substrate as well as methods of removing an immersion layer from a photoresist layer.

### Background Of The Invention

5 To satisfy the ever-increasing desire for faster and smaller electronic devices such as personal computers, it has become desirable to increase the number of microelectronic devices such transistors on a chip without increasing the size of the chip. Accordingly, it is desirable to continually strive to reduce the size of the microelectronic devices.

10 One of the primary hurdles in achieving the much sought after size reduction of microelectronic devices is in the area of photolithography. For decades, photolithography has been utilized to pattern photoresists in the manufacture of microelectronic devices. The resolution of the image formed on a photoresist layer using photolithography generally is directly proportional to the wavelength of the radiation source ( $\lambda$ ) and inversely proportional to the numerical aperture (NA) of the photolithography apparatus. Thus, in order to reduce  
15 the feature size that can be patterned by a photolithography apparatus, it may be desirable to utilize radiation sources having shorter and shorter wavelengths and/or develop photolithography apparatus having larger numerical apertures.

Efforts have resulted in the reduction in wavelength from mercury g line (436 nm) to 193 nm using an excimer laser and further to 157 nm. Research is currently being performed  
20 to further reduce the wavelength of the radiation source using x-ray lithography and/or extreme ultraviolet (EUV) lithography. The cost of continuing to reduce the wavelength of the radiation source may be enormous. New materials for photomasks and/or lenses may need to be developed. As the wavelength becomes shorter, the photolithography method may need to shift from refractive photolithography to reflective photolithography. Designing an

all-reflective camera that achieves lithographic-quality imaging may be more difficult than designing a refractive imaging system because mirrors generally have fewer degrees of freedom to vary than do lenses.

These challenges have resulted in an interesting intersection between microelectronic device manufacture and biology. When faced with the problem of increasing the resolution of microscope lenses beyond their normal magnification, biologists began placing a layer of oil between the lens and the slide to be examined. This technique, known as immersion oil microscopy, reduces the loss of image quality that would occur as a result of the difference in the refractive index between the glass of the lens and air. In an ideal situation, the refractive index of the oil is precisely matched to that of the glass so that the loss of image quality can be eliminated.

Using the principles of immersion oil microscopy, photolithographers have begun to explore an area that is coming to be known as immersion lithography. In immersion lithography, the space between the final optical element and the substrate to be patterned is at least partially filled with a high index medium. M. Switkes & M. Rothschild, "Immersion Lithography at 157 nm," J. Vac. Sci. Technol. B, 19(6): 2353-2356 (Nov/Dec 2001) proposes the use of commercially available perfluoropolyethers (PFPE's), which are widely available as oils and lubricants, for example under the trade name Fomblin® (Solvay Solexis Corp.) as the high index medium in an immersion interference lithography system. Switkes & Rothschild utilized organic solvents such as Fomblin® PFS-1 to remove them from the patterned substrate. The Switkes & Rothschild publication is hereby incorporated herein by reference in its entirety as if set forth fully herein.

Immersion lithography has been regarded as a breakthrough technology that may allow the integration density of integrated circuit devices to continue to increase without the need for post-optical next generation lithography. See, for example, the publication entitled "'Liquid Immersion' could delay post-optical lithography, says MIT", by Mark LaPedus, Semiconductor Business News, March 11, 2002, and the publication entitled "What's Next: Full Immersion Lithography?" Solid State Technology, May 2002, Vol. 45, No. 5, p. 24.

### **Summary Of The Invention**

Embodiments of the present invention provide methods of patterning a substrate by performing immersion lithography on a photoresist layer on the substrate using carbon

dioxide. It has been found, according to some embodiments of the present invention, that supercritical and/or liquid carbon dioxide may be used at various steps in an immersion lithography process and, thereby, replace the use of some or all solvents that have been heretofore been used to deposit the immersion fluid, to remove the immersion fluid and/or to perform various other steps in immersion lithography. The use of organic solvents in immersion photolithography may have a large environmental and/or economic impact on the immersion lithography process. In contrast, embodiments of the invention can reduce or eliminate the need for such organic solvents.

In some embodiments of the present invention, immersion lithography is performed on a photoresist layer on a substrate by providing an immersion layer on the photoresist layer, imaging the photoresist layer through the immersion layer, removing the immersion layer from the photoresist layer, developing the photoresist layer from which the immersion layer has been removed, drying the photoresist layer from which the immersion layer has been removed, patterning the substrate using the photoresist layer that has been developed and removing the photoresist layer from the substrate that has been patterned. According to embodiments of the present invention, one or more of the steps of providing an immersion layer, removing the immersion layer, developing the photoresist layer, drying the photoresist layer and removing the photoresist layer is performed using carbon dioxide.

In some embodiments, carbon dioxide is used in providing an immersion layer on the photoresist layer. In some embodiments, a fluid layer is deposited onto the photoresist layer, wherein the fluid layer comprises carbon dioxide and at least one immersion compound. At least some of the carbon dioxide is then removed from the fluid layer to provide an immersion fluid layer on the photoresist layer.

In other embodiments, carbon dioxide is used to remove an immersion layer from a photoresist layer. In some of these embodiments, an immersion layer is formed on the photoresist layer and the photoresist layer is imaged through the immersion layer. The immersion layer is removed from the imaged photoresist by contacting the immersion layer with an immersion rinse composition that comprises liquid and/or supercritical carbon dioxide.

In still other embodiments, carbon dioxide is used to dry a photoresist layer. In some embodiments, an immersion layer is formed on the photoresist layer, the photoresist layer is imaged through the immersion layer and the immersion layer is removed from the photoresist



layer. The photoresist layer from which the immersion layer has been removed is dried using liquid and/or supercritical carbon dioxide.

In yet other embodiments, carbon dioxide is used to develop the photoresist layer. In particular, in some embodiments, an immersion layer is formed on the photoresist layer, the photoresist layer is imaged through the immersion layer and the immersion layer is removed from the photoresist layer. The photoresist layer from which the immersion layer has been removed is developed using liquid and/or supercritical carbon dioxide. In other embodiments, the immersion layer is removed from the photoresist layer and the photoresist layer is simultaneously developed using liquid and/or supercritical carbon dioxide.

In still other embodiments of the present invention, carbon dioxide is used to remove the photoresist layer and/or clean the substrate after the substrate has been patterned. In particular, in some embodiments, an immersion layer is formed on the photoresist layer, the photoresist layer is imaged through the immersion layer and the immersion layer is removed from the photoresist layer. The photoresist layer from which the immersion layer has been removed is developed and the substrate is patterned using the photoresist layer that has been developed. The photoresist layer is then removed from the substrate that has been patterned using liquid and/or supercritical carbon dioxide.

In still other embodiments, a solid immersion film is placed on (contacted to) the photoresist layer and the photoresist layer is imaged through the solid immersion film. In some embodiments, the solid immersion film includes carbon dioxide and at least one solid immersion film compound. However, in other embodiments, the solid immersion film need not comprise carbon dioxide. Moreover, in still other embodiments, an immersion fluid layer is first formed on the photoresist layer and the solid immersion film is then placed on the immersion fluid layer opposite the photoresist layer. The immersion fluid layer between the solid immersion film and the photoresist layer can improve the contact between the solid immersion film and the photoresist layer. The immersion fluid layer may include carbon dioxide in some embodiments, but need not include carbon dioxide in other embodiments. Thus, some embodiments of the present invention provide the use of solid immersion films, also referred to herein as contact immersion films, in immersion lithography, with or without an intervening immersion fluid layer.

### **Brief Description of the Drawings**

**Figure 1** is a flowchart of methods of patterning a substrate according to various embodiments of the present invention, and includes cross-sectional views of substrates that are patterned according to various embodiments of the present invention corresponding to blocks of the flowchart.

**Figures 2A-2B** are cross-sectional views of substrates that are patterned according to other embodiments of the present invention.

**Figures 3A-3B** are cross-sectional views of substrates that are patterned according to yet other embodiments of the present invention.

**Figure 4** illustrates an immersion interference lithography apparatus that can be employed in performing methods according to embodiments of the present invention; and

**Figure 5** illustrates a semiconductor processing apparatus that can be employed in performing methods according to embodiments of the present invention.

### **Detailed Description Of Preferred Embodiments**

The present invention now will be described more fully hereinafter with reference to the accompanying drawings, in which embodiments of the invention are shown. However, this invention should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. In the drawings, the thickness of layers and regions are exaggerated for clarity. Like numbers refer to like elements throughout. It will be understood that when an element such as a layer, region or substrate is referred to as being "on" or extending "onto" another element, it can be directly on or extend directly onto the other element or intervening elements may also be present. In contrast, when an element is referred to as being "directly on" or extending "directly onto" another element, there are no intervening elements present.

**Figure 1** is a flowchart of methods of patterning a substrate according to embodiments of the present invention, and includes cross-sectional views of substrates that are patterned according to various embodiments of the present invention corresponding to blocks of the flowchart. Referring now to **Figure 1**, a substrate is patterned according to embodiments of the present invention by performing immersion lithography on a photoresist layer on a substrate using carbon dioxide. As shown in **Figure 1**, the substrate **100** may

comprise a semiconductor substrate **100a** and may also include one or more layers **100b** on the semiconductor substrate **100a**. As is well known to those having skill in the art, the semiconductor substrate **100a** may include a monocrystalline, single element and/or compound semiconductor substrate and/or a monocrystalline, single element and/or compound semiconductor layer, such as an epitaxial layer, thereon. The layer **100b** may include one or more insulating layers such as silicon dioxide, silicon nitride and/or other conventional insulating layers, one or more conductive layers, such as a metal and/or doped polysilicon layer and/or any other conventional layer that is used microelectronic device manufacturing. In order to pattern the substrate **100** including patterning the semiconductor substrate **100a** and/or patterning a layer **100b**, a photoresist layer **110** is provided on a substrate **100**, using conventional techniques.

Referring to Block **130**, an immersion layer **120**, also referred to herein as an immersion fluid layer, is provided on the photoresist layer **110**. In some embodiments of the invention, the immersion layer **120** is provided using carbon dioxide **132** by depositing a fluid layer onto the photoresist layer **110**, the fluid layer comprising carbon dioxide and at least one immersion compound. At least some of the carbon dioxide is then removed from the fluid layer to provide an immersion fluid layer **120** on the photoresist layer **110**. In some embodiments, the fluid layer comprises liquid and/or supercritical carbon dioxide. In other embodiments, the at least one immersion fluid compound comprises a fluorine and/or silicon containing compound such as a perfluoropolyether compound. In other embodiments, the at least one immersion fluid compound comprises a polymer. Many examples will be provided below.

Referring again to **Figure 1**, at Block **140**, the photoresist layer is imaged through the immersion layer to produce an imaged photoresist layer **110a**. Imaging may be performed using known immersion lithography processes, such as described in the above-cited Switkes & Rothschild publication. Then, at Block **150**, the immersion layer **120** is removed from the imaged photoresist layer **110a**. In some embodiments, CO<sub>2</sub> **152** is used during the process of removing the immersion layer **120** from the imaged photoresist layer **110a** at Block **150**. In particular, in some embodiments, the immersion layer is contacted with an immersion rinse composition comprising liquid and/or supercritical carbon dioxide as will be described in detail below.

Referring again to **Figure 1**, at Block 160, the photoresist layer 110b is developed and dried to produce a patterned photoresist layer 110c. In some embodiments, CO<sub>2</sub> 162 is used during the process of developing and/or drying the photoresist layer. In particular, in some embodiments, the photoresist layer from which the immersion layer has been removed is dried using liquid and/or supercritical carbon dioxide. In still other embodiments, the photoresist layer from which the immersion layer has been removed is developed using liquid and/or supercritical carbon dioxide 162. In yet other embodiments, carbon dioxide is used to develop and dry the photoresist layer. In still other embodiments, carbon dioxide is used to simultaneously develop and dry the photoresist layer. Techniques for drying and/or developing photoresist using carbon dioxide are known to those having skill in the art and need not be described further herein.

Referring again to **Figure 1**, at Block 170, the substrate is patterned using conventional patterning techniques such as wet and/or dry etching. A patterned layer 100c is thereby produced. Then, at Block 180, the patterned photoresist layer 110c is removed. In some embodiments of the invention, liquid and/or supercritical carbon dioxide is used to remove the patterned photoresist layer 110c from the substrate 100. Techniques for removing photoresist using carbon dioxide are known to those having skill in the art and need not be described further herein.

**Figures 2A-2B** are cross-sectional views illustrating other embodiments of providing an immersion layer on a photoresist layer (Block 130 of **Figure 1**) according to the present invention. As shown in **Figure 2A**, a solid immersion film 220 is placed on (contacted to) the photoresist layer 110 to form a solid immersion film, as shown in **Figure 2B**. The composition of the solid immersion film 220 will be described below. The solid immersion film 220 may be attached using standard techniques for placing a solid thin film on a substrate. In some embodiments, the solid immersion film 220 comprises carbon dioxide and at least one solid immersion film compound. Then, as was described above in connection with Block 130, the carbon dioxide is removed from the solid immersion film. In other embodiments, a solid immersion film may be used to pattern a substrate in an immersion lithography process without using CO<sub>2</sub>. Accordingly, solid immersion lithography may be provided, with or without using carbon dioxide in the process.

**Figures 3A-3B** are cross-sectional views of immersion lithography processes according to yet other embodiments of the present invention. In these embodiments, an

immersion fluid layer 330 is interposed between the solid immersion film 320, which may be similar to the solid immersion film 220 of Figure 2A, and the photoresist 110, to promote enhanced contact and/or a more uniform optical interface between the solid immersion film 320 and the photoresist 110. Figure 3B illustrates a solid immersion film 320 on the photoresist 110 with an immersion fluid layer 330 therebetween. In some embodiments, the solid immersion film 320 is substantially thicker than the immersion fluid layer 320, so that the immersion lithography parameters are governed primarily by the solid immersion film 320. In other embodiments, differing thickness ratios may be used. In still other embodiments, the use of a solid immersion film 320 and a liquid immersion layer 330 may be used in immersion lithography processes that do not involve CO<sub>2</sub>. It will be understood that conventional immersion lithography and/or immersion lithography of Figure 1 may then be performed on embodiments of Figures 2B and/or 3B.

Additional discussion of various embodiments of the present invention now will be described.

According to some embodiments of the present invention, a method of patterning a photoresist layer on a substrate includes depositing a fluid layer, which includes carbon dioxide and at least one immersion compound, onto the photoresist layer and removing the carbon dioxide from the fluid layer to provide an immersion fluid layer on the photoresist layer.

The fluid layer may be deposited on the photoresist layer by various processes as will be understood by those skilled in the art. For example, in some embodiments, the immersion fluid is spin coated on the substrate. In other embodiments, the immersion fluid dissolved in a solvent is spin coated on the substrate, wherein the solvent comprises CO<sub>2</sub>. In other embodiments, a free meniscus coating method such as dip coating and/or knife coating may be used.

The carbon dioxide may be in a liquid, gaseous, or supercritical phase. If liquid CO<sub>2</sub> is used, the temperature employed during the process is below 31°C in some embodiments. If gaseous CO<sub>2</sub> is used, the phase may be employed at high pressure. As used herein, the term "high pressure" generally refers to CO<sub>2</sub> having a pressure from about 50 to about 500 bar. In some embodiments, the CO<sub>2</sub> is utilized in a "supercritical" phase. As used herein, "supercritical" means that a fluid medium is above its critical temperature and pressure, i.e., about 31°C and about 71 bar for CO<sub>2</sub>. The thermodynamic properties of CO<sub>2</sub> are reported in

Hyatt, *J. Org. Chem.* **49**: 5097-5101 (1984); therein, it is stated that the critical temperature of CO<sub>2</sub> is about 31°C; thus in some embodiments of the present invention may be carried out at a temperature above 31°C. For the purposes of the invention, CO<sub>2</sub> at a pressure ranging from at a lower end of about 20 or about 50 bar to an upper end of about 200 bar or about 1000 bar  
5 may be employed.

The immersion fluid compound may be selected from various immersion fluid compounds including, but not limited to, perfluoropolyethers and other suitable fluorinated compounds. Other suitable fluorinated compounds may include fluoroalkyl (meth)acrylate homo- and copolymers, homo- and copolymers of tetrafluoroethylene, hexafluoropropylene,  
10 perfluorodimethyldioxole, norbornene, vinylidene fluoride and norbornene derivatives, as described for example in published International Patent Application Nos. WO 00/17712 and WO 00/67072. The material also may contain silicon or siloxane units such as polydimethylsiloxane or polydialkylsilanes. These materials may be CO<sub>2</sub> soluble, so that they can be soluble deposited in CO<sub>2</sub>. In general, the immersion fluid compound should be  
15 transparent enough to allow a working distance between a final optical element and a microelectronic workpiece of at least 10 µm. The immersion fluid compound should not interact with the photoresist such that it would impede image formation. In addition, the immersion fluid compound should be compatible with the clean room environment and the semiconductor manufacturing process. In some embodiments, the immersion fluid  
20 compound is nontoxic and/or is chemically inert.

In other embodiments, the immersion fluid may also take the form of a contact film of a high transparency material that may be derived from the materials listed above, including a crosslinked material such as a crosslinked PFPE film. In still other embodiments, the immersion fluid may take the form of a contact film as described above, and an interposed  
25 liquid immersion layer of the type described above.

In some embodiments, the immersion fluid compound is resistant to damage by radiation (e.g., lasers) from sources that are used for photolithography. The resistance of the immersion fluid compound to damage by radiation sources can be determined by measuring the change in transmission for the compound following exposure to the radiation source of  
30 interest. For example, a layer of the immersion fluid compound can be placed between two CaF<sub>2</sub> windows and irradiated at 157 nm using a standard dose, such as 100 J/cm at a fluence of 0.3 mJ/cm<sup>2</sup>-pulse and the change in transmission measured for the compound. In some

embodiments, particularly those in which the immersion fluid compound is to be used for multiple exposures, the change in transmission may be less than 50 percent and in other embodiments may be less than 25 percent. While the immersion fluid compound is preferably resistant to damage by the radiation source of interest, immersion fluid compounds of the present invention may still be utilized if they are easily damaged by the radiation source of interest. In these cases, the immersion fluid compound can be replaced after 1, 2, 3, 4, or 5 exposures. For example, an immersion fluid compound that is easily damaged by the radiation source of interest could travel with the wafer, providing fresh immersion fluid compound for each exposed field.

The carbon dioxide can be removed from the fluid layer to provide the immersion fluid layer by various processes as will be understood by those skilled in the art including, but not limited to, reducing the pressure of the fluid layer and/or increasing the temperature of the fluid layer. Because the microelectronic workpiece typically has a thermal budget, it may be desirable in some embodiments to remove the carbon dioxide from the fluid layer by reducing the pressure of the fluid layer.

In some embodiments, the refractive index of the immersion fluid layer should be within 10 to 20 percent of the refractive index for the optics of the imaging apparatus. For example, if  $\text{CaF}_2$  optics ( $n = 1.56$ , where  $n$  is the refractive index) are used in the imaging apparatus, the immersion fluid compound can have a refractive index between a lower limit of 1.25 or 1.40 and an upper limit of 1.72 or 1.87.

In some embodiments, methods of patterning a photoresist layer according to the present invention include placing the substrate having a photoresist layer thereon into a carbon dioxide chamber prior to the depositing of the immersion fluid layer. The carbon dioxide chamber is a chamber that can withstand the pressures and temperatures for processing with liquid or supercritical carbon dioxide, as described above. The carbon dioxide chamber may be on a track. As is well known to those having skill in the art, microelectronic devices may be fabricated using an ensemble of tools on a track. A  $\text{CO}_2$  chamber can be added to the track to perform immersion lithography according to some embodiments of the present invention.

In some embodiments, the carbon dioxide chamber is a part of a microelectronic device processing apparatus, such as the one illustrated in **Figure 5**. The apparatus includes a loadlock chamber **510** having a cassette **520** loaded with one or more semiconductor wafers

530 (a semiconductor substrate). The loadlock chamber 510 is connected to a transfer chamber 560. The transfer chamber 560 may be used to transfer the semiconductor wafer 530 from a first chamber within the apparatus to a second chamber within the apparatus. While the transfer chamber 560 as illustrated in Figure 5 has robot arms 550 for loading and unloading the semiconductor wafer 530, it is to be understood that various means for loading and unloading the semiconductor wafer 530 may be used. As shown in Figure 5, the transfer chamber 560 is connected to a carbon dioxide chamber 540.

In some embodiments of the present invention, a method of patterning a photoresist layer includes contacting the immersion fluid layer with an immersion rinse composition (Block 150 of Figure 1). The contacting of the immersion fluid layer with the immersion rinse composition may be performed by various processes as will be understood by those in the art including, but not limited to, rinsing with a solvent such as CFCs, HCFCs, HFCs and FCs, or a non-molecular etchant, PFP solvent or fluoroether. In some embodiments, the contacting of the immersion fluid layer with an immersion rinse composition is performed in a carbon dioxide chamber. The carbon dioxide chamber is a chamber that can withstand the pressures and temperatures for processing with liquid or supercritical carbon dioxide, as described above. In some embodiments, the carbon dioxide chamber is on a track. When a carbon dioxide chamber is used for depositing the immersion fluid layer and a carbon dioxide chamber is used for removing the immersion fluid layer, the carbon dioxide chamber utilized for the depositing the immersion fluid layer may be the same carbon dioxide chamber utilized for removal of the immersion fluid layer or may be a different carbon dioxide chamber.

The immersion rinse composition is a composition capable of removing all or substantially all of the immersion fluid layer from the patterned photoresist layer. The immersion rinse composition may be an aqueous composition, an organic composition, or a carbon-dioxide based (e.g., comprising greater than 50 percent carbon dioxide) composition. The immersion rinse composition comprises liquid or supercritical carbon dioxide in some embodiments, as described above.

In some embodiments, the immersion rinse composition comprises liquid or supercritical carbon dioxide and a co-solvent. Exemplary co-solvents that could be used include, but are not limited to, alcohols (e.g., methanol, ethanol, and isopropanol); fluorinated and other halogenated solvents (e.g., chlorotrifluoromethane, trichlorofluoromethane, perfluoropropane, chlorodifluoromethane, and sulfur hexafluoride); amines (e.g., N-methyl



pyrrolidone); amides (e.g., dimethyl acetamide); aromatic solvents (e.g., benzene, toluene, and xylenes); esters (e.g., ethyl acetate, dibasic esters, and lactate esters); ethers (e.g., diethyl ether, tetrahydrofuran, and glycol ethers); aliphatic hydrocarbons (e.g., methane, ethane, propane, ammonium butane, n-pentane, and hexanes); oxides (e.g., nitrous oxide); olefins (e.g., ethylene and propylene); natural hydrocarbons (e.g., isoprenes, terpenes, and d-limonene); ketones (e.g., acetone and methyl ethyl ketone); organosilicones; alkyl pyrrolidones (e.g., N-methyl pyrrolidone); paraffins (e.g., isoparaffin); petroleum-based solvents and solvent mixtures; and any other compatible solvent or mixture that is available and suitable. Mixtures of the above co-solvents may be used.

According to still other embodiments of the present invention, a method of patterning a photoresist layer on a substrate includes depositing an immersion fluid layer onto the photoresist layer, imaging the photoresist layer to provide an imaged photoresist layer, and contacting the immersion fluid layer with an immersion rinse composition, which includes liquid or supercritical carbon dioxide, to remove the immersion fluid layer from the imaged photoresist layer.

The immersion fluid layer may be deposited on the photoresist layer as described above at Block 130. The immersion fluid layer may include various immersion fluid compounds including, but not limited to, perfluoropolyethers. In some embodiments, the immersion fluid layer is Fomblin<sup>®</sup> Y (e.g., Fomblin<sup>®</sup> Y-18 or Fomblin<sup>®</sup> Y-140) or Fomblin<sup>®</sup> Z (e.g., Fomblin<sup>®</sup> Z-25) commercially available from Solvay Solexis of Thorofare, New Jersey. In other embodiments, the immersion fluid layer is a perfluoropolyether or other suitable fluorinated compound layer that has been deposited utilizing carbon dioxide as described above. The immersion fluid compound and/or immersion fluid layer may have similar characteristics to one or more of the various characteristics described above with respect to immersion fluid compounds and immersion fluid layers such as transparency, freedom from optical defects, minimal or no interaction with the resist to impede image formation, compatibility with the clean room environment and the semiconductor manufacturing process, not toxic, chemically inert, resistant to damage by the radiation of interest, and/or index matched with the final optical element.

After depositing the immersion fluid layer, the photoresist layer may be imaged utilizing various immersion lithography processes (Block 140). In general, "dry" (i.e., non-immersion) lithography apparatus can be converted to immersion lithography processes by,

for example, introducing a layer of immersion fluid between, for example, the final optical element and the photoresist layer on the semiconductor substrate. For example, as illustrated in **Figure 4**, an interference lithography system **400** will now be described. The interference lithography system **400** may be a conventional interference lithography system as will be understood by those skilled in the art with the exception that an immersion fluid layer **460** has been deposited between the final optical element **450** and the microelectronic workpiece **470**, which comprises a substrate with a photoresist layer thereon, where the photoresist layer is adjacent the immersion fluid layer. In general, a radiation source **410** such as a Lambda-Physik LPX-200 F<sub>2</sub> laser emits a laser beam **420**. The laser beam **420** is split into two polarized arms by partial reflection from the reflecting plates **430**, which may comprise, for example, CaF<sub>2</sub>. The arms are then reflected in the mirrors **440**, which may comprise, for example, Si, and eventually enter the final optical element **450**. The arms then pass through the immersion fluid layer **460** and intersect at the surface of the microelectronic workpiece **470**. While embodiments of the present invention have been described with reference to an interference lithography system, it is to be understood that the present invention may be performed utilizing various lithography systems as will be understood by those skilled in the art including, but not limited to, projection lithography and/or contact printing lithography.

After imaging the photoresist layer, the immersion layer is removed (Block **160**) by contacting the immersion layer with an immersion rinse composition as described above.

According to other embodiments of the present invention, a method of removing an immersion fluid layer from an imaged photoresist layer on a substrate includes contacting the immersion fluid layer with an immersion rinse composition comprising liquid or supercritical carbon dioxide to remove the immersion fluid layer from the imaged photoresist layer. The contacting operation, immersion fluid layer, and immersion rinse composition can be similar to those described above.

In still other embodiments, as was described above, an immersion fluid is deposited, the photoresist is imaged and the immersion fluid is rinsed off. The photoresist is developed, for example, using TMAH and/or other conventional developer. Then, the patterned photoresist is dried using CO<sub>2</sub> and/or CO<sub>2</sub> with surfactants. By using CO<sub>2</sub> and/or CO<sub>2</sub> with surfactants, image collapse can be reduced or prevented. In still other embodiments, development may take place directly using CO<sub>2</sub> for negative or positive tone images using techniques that are known to those having skill in the art.

In still other embodiments, non-CO<sub>2</sub> methods may be used for applying and removing the immersion fluid, but then CO<sub>2</sub> may be used to assist in developing the pattern in the resist, either using CO<sub>2</sub> directly to develop the pattern or using standard development methods followed by CO<sub>2</sub>-based drying methods. CO<sub>2</sub> may be used to simultaneously  
5 develop the photoresist layer and remove the immersion layer in other embodiments. In still other embodiments, as was described above, the photoresist is cleaned or removed using carbon dioxide.

In still other embodiments, the immersion fluid is a polymeric film and is physically placed onto the photoresist, with or without using carbon dioxide. In still other embodiments,  
10 a liquid is placed between the polymeric film and the photoresist with or without the use of carbon dioxide.

In the specification, there has been disclosed embodiments of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being set forth in the following  
15 claims.

**That Which is Claimed is:**

1. A method of patterning a substrate comprising:  
performing immersion lithography on a photoresist layer on the substrate using carbon dioxide.
2. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on the substrate using carbon dioxide comprises:  
providing an immersion layer on the photoresist layer;  
imaging the photoresist layer through the immersion layer;  
removing the immersion layer from the photoresist layer;  
developing the photoresist layer from which the immersion layer has been removed;  
drying the photoresist layer from which the immersion layer has been removed;  
patterning the substrate using the photoresist layer that has been developed; and  
removing the photoresist layer from the substrate that has been patterned;  
wherein one or more of the providing an immersion layer, removing the immersion layer, developing the photoresist layer, drying the photoresist layer and removing the photoresist layer is performed using carbon dioxide.
3. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on the substrate using carbon dioxide comprises:  
depositing a fluid layer onto the photoresist layer, the fluid layer comprising carbon dioxide and at least one immersion compound; and  
removing at least some of the carbon dioxide from the fluid layer to provide an immersion fluid layer on the photoresist layer.
4. A method according to Claim 3 wherein the fluid layer comprises liquid and/or supercritical carbon dioxide.
5. A method according to Claim 3 wherein the at least one immersion fluid compound comprises a fluorine and/or silicon-containing compound.

6. A method according to Claim 5 wherein the fluorine and/or silicon-containing compound comprises a perfluoropolyether compound.

7. A method according to Claim 3 wherein the at least one immersion fluid compound comprises a polymer.

8. A method according to Claim 3 wherein the depositing a fluid layer is performed in a carbon dioxide chamber.

9. A method according to Claim 8 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.

10. A method according to Claim 2 wherein the drying is performed prior to the developing.

11. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:  
forming an immersion layer on the photoresist layer;  
imaging the photoresist layer through the immersion layer; and  
removing the immersion layer from the imaged photoresist layer by contacting the immersion layer with an immersion rinse composition comprising liquid and/or supercritical carbon dioxide.

12. A method according to Claim 11 wherein the forming an immersion layer comprises:  
depositing a fluid layer onto the photoresist layer, the fluid layer comprising carbon dioxide and at least one immersion fluid compound; and  
removing the carbon dioxide from the fluid layer to provide the immersion layer on the photoresist layer.

13. A method according to Claim 12 wherein the fluid layer comprises liquid and/or supercritical carbon dioxide.

14. A method according to Claim 12 wherein the at least one immersion fluid compound comprises a fluorine and/or silicon-containing compound.
15. A method according to Claim 14 wherein the fluorine and/or silicon-containing compound comprises a perfluoropolyether compound.
16. A method according to Claim 12 wherein the at least one immersion fluid compound comprises a polymer.
17. A method according to Claim 12 wherein the depositing a fluid layer is performed in a carbon dioxide chamber.
18. A method according to Claim 17 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.
19. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:  
forming an immersion layer on the photoresist layer;  
imaging the photoresist layer through the immersion layer;  
removing the immersion layer from the photoresist layer; and  
drying the photoresist layer from which the immersion layer has been removed using liquid and/or supercritical carbon dioxide.
20. A method according to Claim 19 wherein the drying is performed in a carbon dioxide chamber.
21. A method according to Claim 20 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.
22. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:

forming an immersion layer on the photoresist layer;  
imaging the photoresist layer through the immersion layer;  
removing the immersion layer from the photoresist layer; and  
developing the photoresist layer from which the immersion layer has been removed  
using liquid and/or supercritical carbon dioxide.

23. A method according to Claim 22 wherein the developing is performed in a carbon dioxide chamber.

24. A method according to Claim 23 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.

25. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:  
forming an immersion layer on the photoresist layer;  
imaging the photoresist layer through the immersion layer; and  
removing the immersion layer from the photoresist layer and simultaneously developing the photoresist layer using liquid and/or supercritical carbon dioxide.

26. A method according to Claim 25 wherein the removing and simultaneously developing is performed in a carbon dioxide chamber.

27. A method according to Claim 8 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.

28. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:  
forming an immersion layer on the photoresist layer;  
imaging the photoresist layer through the immersion layer;  
removing the immersion layer from the photoresist layer;  
developing the photoresist layer from which the immersion layer has been removed;  
patterning the substrate using the photoresist layer that has been developed; and

removing the photoresist layer from the substrate that has been patterned using liquid and/or supercritical carbon dioxide.

29. A method according to Claim 28 wherein the removing is performed in a carbon dioxide chamber.

30. A method according to Claim 26 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.

31. A method according to Claim 1 wherein the performing immersion lithography on a photoresist layer on a substrate using carbon dioxide comprises:  
placing a solid immersion film on the photoresist layer; and  
imaging the photoresist layer through the solid immersion film.

32. A method according to Claim 31 wherein the placing a solid immersion film on the photoresist layer comprises:  
placing a solid immersion film comprising carbon dioxide and at least one solid immersion film compound on the photoresist layer; and  
removing the carbon dioxide from the solid immersion film.

33. A method according to Claim 31 wherein the placing a solid immersion film on the photoresist layer is preceded by placing an immersion fluid layer on the photoresist layer and wherein the placing a solid immersion film on the photoresist layer comprises placing a solid immersion film on the immersion fluid layer opposite the photoresist layer.

34. A method according to Claim 33 wherein the placing an immersion fluid layer comprises:  
depositing a fluid layer onto the photoresist layer, the fluid layer comprising carbon dioxide and at least one immersion compound; and  
removing at least some of the carbon dioxide from the fluid layer to provide an immersion fluid layer on the photoresist layer.



35. A method according to Claim 34 wherein the fluid layer comprises liquid and/or supercritical carbon dioxide.

36. A method according to Claim 34 wherein the at least one immersion fluid compound comprises a fluorine and/or silicon-containing compound.

37. A method according to Claim 36 wherein the fluorine and/or silicon-containing compound comprises a perfluoropolyether compound.

38. A method according to Claim 34 wherein the at least one immersion fluid compound comprises a polymer.

39. A method according to Claim 34 wherein the depositing a fluid layer is performed in a carbon dioxide chamber.

40. A method according to Claim 39 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.

41. A method of patterning a substrate comprising:  
placing a solid immersion film on a photoresist layer on a substrate; and  
imaging the photoresist layer through the solid immersion film that was placed on the photoresist layer.

42. A method according to Claim 71 wherein the placing a solid immersion film on the photoresist layer is preceded by placing a liquid immersion layer on the photoresist layer and wherein the placing a solid immersion film on the photoresist layer comprises placing a solid immersion film on the liquid immersion layer opposite the photoresist layer.

43. A method according to Claim 42 wherein the placing an immersion fluid layer comprises:

depositing a fluid layer onto the photoresist layer, the fluid layer comprising carbon dioxide and at least one immersion compound; and

removing at least some of the carbon dioxide from the fluid layer to provide an immersion fluid layer on the photoresist layer.

44. A method according to Claim 43 wherein the fluid layer comprises liquid and/or supercritical carbon dioxide.

45. A method according to Claim 43 wherein the at least one immersion fluid compound comprises a fluorine and/or silicon-containing compound.

46. A method according to Claim 45 wherein the fluorine and/or silicon-containing compound comprises a perfluoropolyether compound.

47. A method according to Claim 43 wherein the at least one immersion fluid compound comprises a polymer.

48. A method according to Claim 43 wherein the depositing a fluid layer is performed in a carbon dioxide chamber.

49. A method according to Claim 48 wherein the carbon dioxide chamber comprises part of a microelectronic processing track.

1/3

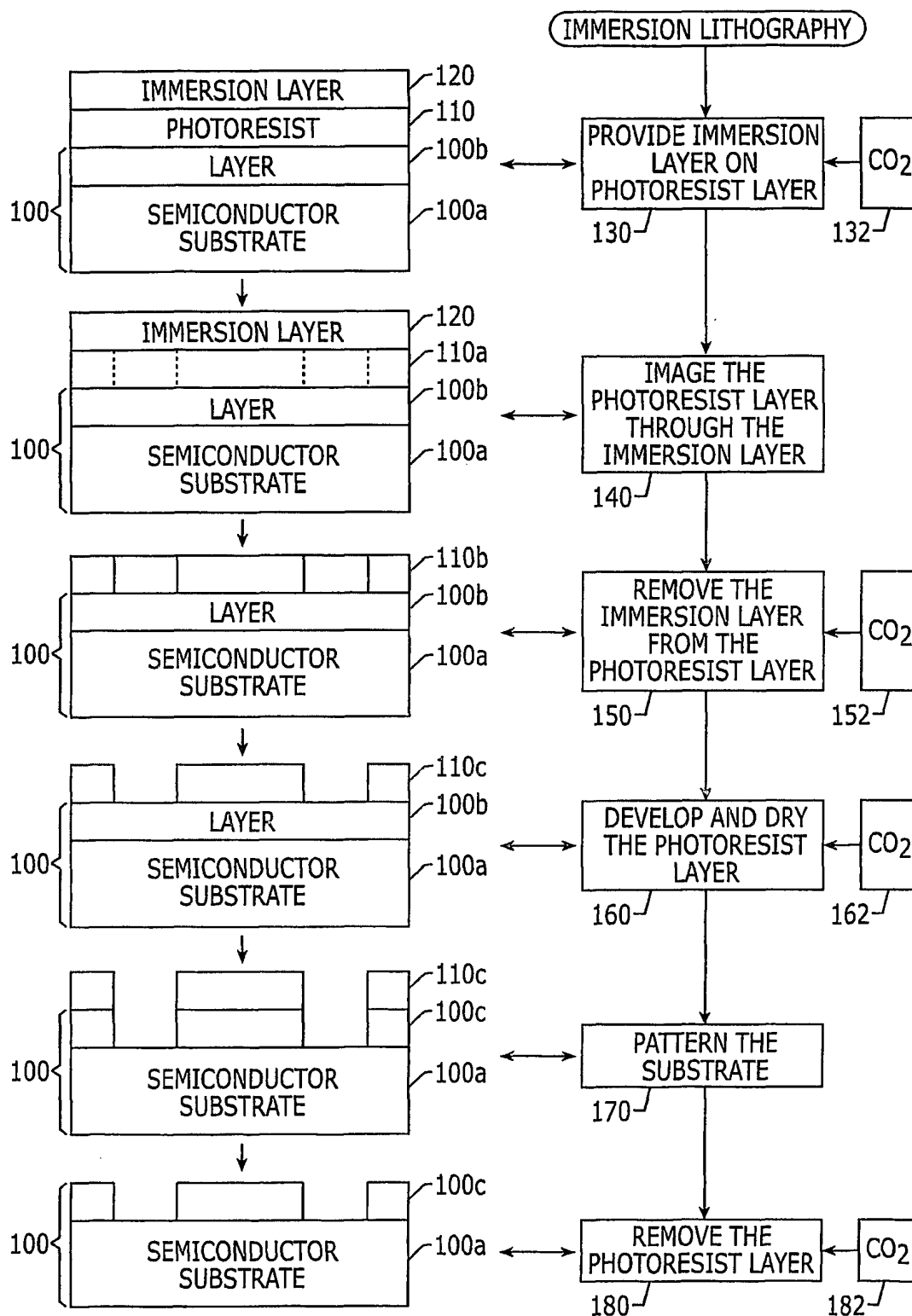


FIG. 1

2/3

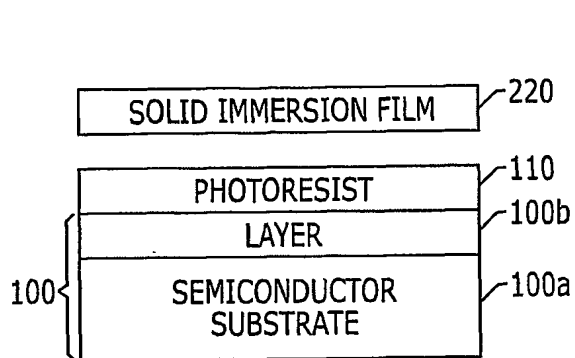


FIG. 2A

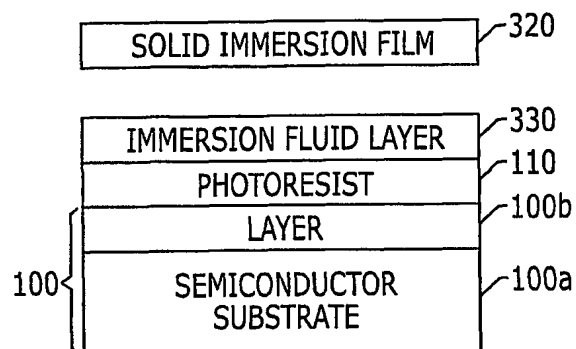


FIG. 3A

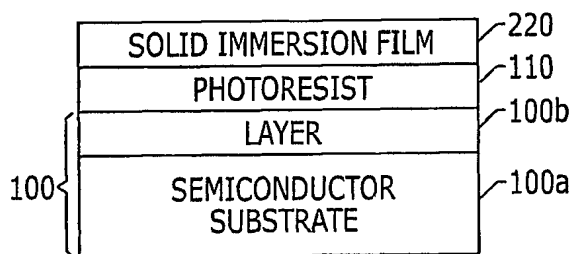


FIG. 2B

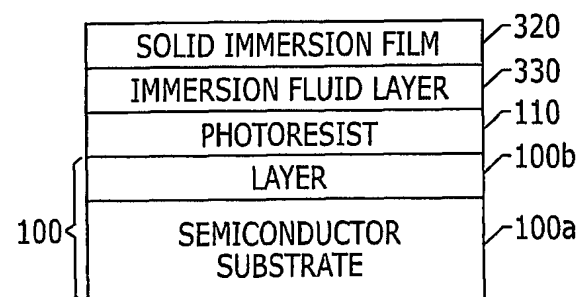


FIG. 3B

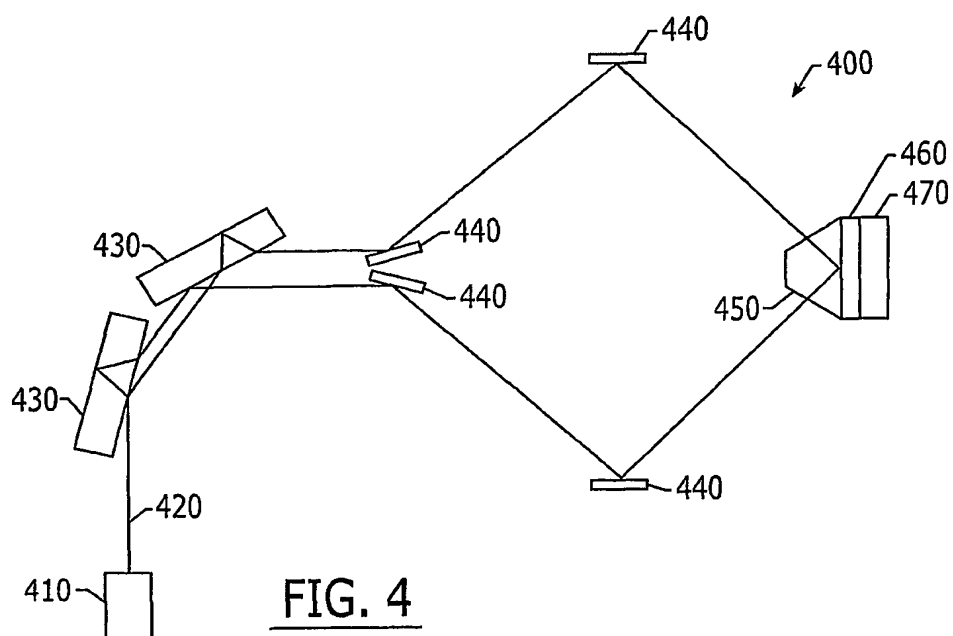


FIG. 4

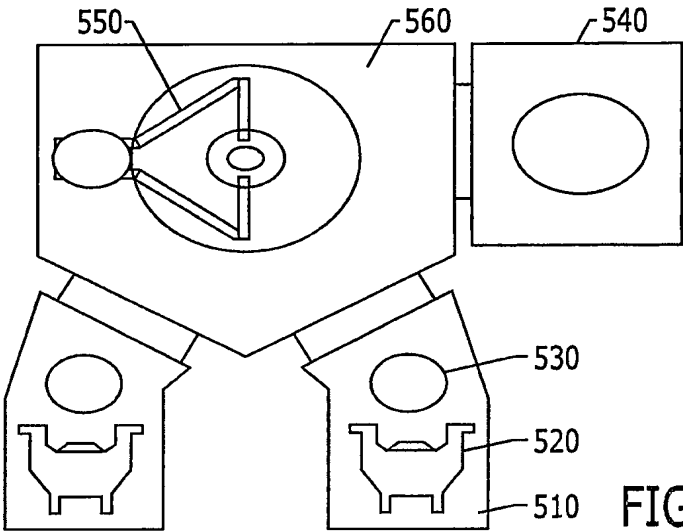


FIG. 5

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/003556

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 G03F7/20

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99/01797 A (BATCHELDER JOHN SAMUEL) 14 January 1999 (1999-01-14) page 1, lines 10-25; claims 1,15,17,18; table 1 page 4, lines 15-25 page 9, lines 1-3 page 9, line 9 - page 10, line 22	1-49
X	M. SWITKES, R. R. KUNZ, R. F. SINTA, M. ROTHSCCHILD: "Immersion Liquids for Lithography in the Deep Ultraviolet" PROCEED. OF SPIE, vol. 5040, 25 February 2003 (2003-02-25), pages 690-699, XP002285465 abstract; figure 8 page 693, lines 28-46 ----- -/-	1-49

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

22 June 2004

Date of mailing of the international search report

05/07/2004

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/003556

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	----- PATENT ABSTRACTS OF JAPAN vol. 2000, no. 06, 22 September 2000 (2000-09-22) & JP 2000 085025 A (NIKON CORP), 28 March 2000 (2000-03-28) abstract	1-49
A	----- SWITKES M ET AL: "RESOLUTION ENHANCEMENT OF 157 NM LITHOGRAPHY BY LIQUID IMMERSION" PROCEEDINGS OF THE SPIE, SPIE, BELLINGHAM, VA, US, vol. 4691, 5 March 2002 (2002-03-05), pages 459-465, XP009014679 ISSN: 0277-786X abstract -----	1-49

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/003556

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